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ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY.

ANNUAL REPORTS

ON THE

PROGRESS OF CHEMISTRY

FOR 1932.

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TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

Abbreviated Title.	Full Title.
A.	Abstracts in Journal of the Chemical Society (until 1925) or in British Chemical Abstracts,* Section A.
Acta Phytochim.	Acta Phytochimica.
Amer. J. Bot.	American Journal of Botany.
Amer. J. Sci.	American Journal of Science.
Amer. Min.	American Mineralogist.
Anal. Asoc. Quím. Argentina	Anales de la Asociación Química Argentina.
Anal. Fís. Quím.	Anales de la Sociedad Espanõla Física y Química.
Analyst	The Analyst.
Angew. Chem.	Angewandte Chemie (formerly Zeitschrift für Angewandte Chemie).
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Acad. Brasil. Sci.	Annales da Academia Brasileira de Sciencias.
Ann. Bot.	Annals of Botany.
Ann. Chim.	Annales de Chimie.
Ann. Chim. analyt.	Annales de Chimie analytique et de Chimie appliquée.
Ann. Chim. Appl.	Annali di Chimica Applicata.
Ann. Inst. Anal. Phys. Chim.	Annales de l'Institut d'Analyse physico-chimique, Leningrad.
Ann. Physik	Annalen der Physik.
Ann. Reports	Annual Reports of the Chemical Society.
Ann. sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy.
Ann. Soc. Sci. Bruxelles	Annales et Bulletin de la Société royale des Sciences médicales et naturelles de Bruxelles.
Arch. Eisenhüttenw.	Archiv für das Eisenhüttenwesen.
Arch. Ist. biochim. ital.	Archivio dell' Istituto biochimico italiano.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. biol., Russia	Archives des Sciences biologiques (U.S.S.R.).
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Arkiv Kemi, Min. Geol.	Arkiv för Kemi, Mineralogi och Geologi.
Atti R. Accad. Lincei	Atti (Rendiconti) della Reale Accademia Nazionale dei Lincei, classe di scienze fisiche, matematiche e naturali, Roma.
B.	British Chemical Abstracts,* Section B.
Ber.	Berichte der deutschen chemischen Gesellschaft.
Ber. deut. bot. Ges.	Berichte der deutschen botanischen Gesellschaft.
Biochem. J.	The Biochemical Journal.
Biochem. Z.	Biochemische Zeitschrift.
Bol. min. Soc. nac. Min.	Boletin minero de la Sociedad nacional de Mineria (Chile).
Bot. Gaz.	The Botanical Gazette.
Brennstoff-Chem.	Brennstoff-Chemie.
Brit. Med. J.	The British Medical Journal.
Bul. Soc. Stiinte Cluj	Buletinul Societătii de Stiinte din Cluj.
Bull. Acad. Polonaise	Bulletin Internationale de l'Académie Polonaise des Sciences et des Lettres.
Bull. Acad. roy. Belg.	Académie royale de Belgique.—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. U.R.S.S.	Bulletin de l'Académie des Sciences de l'Union des Républiques Soviétiques Socialistes.
Bull. Chem. Soc. Japan	Bulletin of the Chemical Society of Japan.
Bull. Comm. géol. Finlande	Bulletin de la Commission géologique de Finlande.
Bull. Inst. Min. Met.	Bulletin of the Institution of Mining and Metallurgy.
Bull. Inst. Phys. Chem. Res. Tokyo	Bulletin of the Institute of Physical and Chemica Research, Tokyo.
Bull. Sericult. Silk Ind. Japan	Bulletin of the Sericulture and Silk Industry, Japan.

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* The year is not inserted in references to 1932.

Abbreviated Title.	FULL TITLE.
Bull. Soc. chim. . . .	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg. . .	Bulletin de la Société chimique de Belgique.
Bull. Soc. Chim. biol. . .	Bulletin de la Société de Chimie biologique.
Bull. Soc. chim. Yougoslav.	Bulletin de la Société chimique du Royaume de Yougoslavie.
Bull. Soc. d'Encour. . .	Bulletin de la Société d'Encouragement pour l'Industrie nationale.
Bull. Soc. franç. Min. .	Bulletin de la Société française de Minéralogie.
Bull. Torrey Bot. Club .	Bulletin of the Torrey Botanical Club.
Bur. Stand. J. Res. . .	Bureau of Standards Journal of Research.
Canadian J. Res. . .	Canadian Journal of Research.
Cellulosechem. . . .	Cellulosechemie. Zeitschrift für Gerüst-, Inkrustations- und andere Begleitstoffe der Cellulose.
Centr. Bakt. Par. . . .	See *Zentr. Bakt. Par.* (spelling changed in 1929).
Centr. Min.	Centralblatt für Mineralogie, Geologie, und Paläontologie.
Céram. et Verrerie . .	Céramique et Verrerie.
Chem. Erde	Chemie der Erde.
Chem. and Ind. . . .	Chemistry and Industry.
Chem. Listy	Chemické Listy pro Vědu a Průmysl. Organ de la "Ceská chemická Společnost pro Vědu a Průmysl."
Chem. News	Chemical News.
Chem. Reviews . . .	Chemical Reviews.
Chem. Rund. Mitteleuropa Balkan	Chemische Rundschau für Mitteleuropa und den Balkan.
Chem. Weekblad . . .	Chemisch Weekblad.
Chem. Zentr. . . .	Chemisches Zentralblatt.
Chem.-Ztg.	Chemiker-Zeitung.
Chim. et Ind. . . .	Chimie et Industrie.
Chinese J. Physiol. . .	Chinese Journal of Physiology.
Coll. Czech. Chem. Comm. .	Collection of Czechoslovak Chemical Communications.
Compt. rend. . . .	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt. rend. Acad. Agric. France	Comptes rendus des Séances de l'Académie d'Agriculture de France.
Compt. rend. Soc. Biol. .	Comptes rendus hebdomadaires de Séances de la Société de Biology.
Contr. Boyce Thompson Inst.	Contributions from Boyce Thompson Institute.
Cornell Univ. Agric. Exp. Sta. Mem.	Cornell University Agricultural Experiment Station Memoirs.
Econ. Geol.	Economic Geology.
Eng. and Min. J.. . .	Engineering and Mining Journal.
Ernähr. Pflanze . . .	Die Ernährung der Pflanze.
Fortschr. Chem. Physik .	Fortschritte der Chemie, Physik und physikalischen Chemie.
Gazzetta	Gazzetta chimica italiana.
Geol. Mag.	The Geological Magazine.
Ges. Abhandl. Kennt. Kohle.	Gesammelte Abhandlungen zur Kenntnis der Kohle.
Giorn. Chim. ind. appl. .	Giornale di Chimica industriale et applicata.
Glastech. Ber. . . .	Glastechnische Berichte.
Helv. Chim. Acta . . .	Helvetica Chimica Acta.
Ind. Chem.	The Industrial Chemist and Chemical Manufacturer.
Ind. chim.	L'Industrie chimica, mineraria e metallurgica.
Ind. Eng. Chem. . . .	Industrial and Engineering Chemistry.
Ind. Eng. Chem. (Anal.) .	Industrial and Engineering Chemistry: Analytica Edition.
Indian J. Physics . .	Indian Journal of Physics.
J.	Journal of the Chemical Society.
J. Agric. Chem. Soc. Japan	Journal of the Agricultural Chemical Society of Japan.
J. Agric. Res. . . .	Journal of Agricultural Research.

Abbreviated Title.	FULL TITLE.
J. Agric. Sci.	The Journal of Agricultural Science.
J. Amer. Ceramic Soc.	Journal of the American Ceramic Society.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Amer. Pharm. Assoc.	Journal of the American Pharmaceutical Association.
J. Amer. Soc. Agron.	Journal of the American Society of Agronomy.
J. Appl. Chem. Russia	Zhurnal prikladnoi Chimii.
J. Biol. Chem.	Journal of Biological Chemistry.
J. Chem. Met. Min. S. Africa	Journal of the Chemical, Metallurgical and Mining Society of South Africa.
J. Chim. physique	Journal de Chimie physique.
J. Counc. Sci. Ind. Res. Australia	Journal of the Council for Scientific and Industrial Research (Australia).
J. Dept. Agric. Kyushu	Journal of the Department of Agriculture, Kyushu Imperial University.
J. Exp. Med.	Journal of Experimental Medicine.
J. Fac. Agric. Hokkaido	Journal of the Faculty of Agriculture, Hokkaido Imperial University.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Gen. Chem. (U.S.S.R.)	Journal of General Chemistry (U.S.S.R.) (formerly chemical part of the Journal of the Physical and Chemical Society of Russia).
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry (now Industrial and Engineering Chemistry).
J. Indian Chem. Soc.	Quarterly Journal of the Indian Chemical Society.
J. Inst. Metals	Journal of the Institute of Metals.
J. Inst. Petrol. Tech.	Journal of the Institute of Petroleum Technologists.
J. Iron Steel Inst.	Journal of the Iron and Steel Institute.
J. Marine Biol. Assoc.	Journal of the Marine Biological Association of the United Kingdom.
J. Path. Bact.	Journal of Pathology and Bacteriology.
J. Pharm. Soc. Japan	Journal of the Pharmaceutical Society of Japan (Yakugakuzasshi).
J. Physical Chem.	The Journal of Physical Chemistry.
J. Physiol.	The Journal of Physiology.
J. Pomology	The Journal of Pomology and Horticultural Science.
J. pr. Chem.	Journal für praktische Chemie.
J. Proc. Roy. Soc. N.S.W.	Journal and Proceedings of the Royal Society of New South Wales.
J. Roy. Soc. W. Australia	Journal of the Royal Society of West Australia.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia (now Journal of General Chemistry, U.S.S.R.).
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Chem. Ind. Japan	Journal of the Society of Chemical Industry, Japan (Kōgyō Kwagaku Zasshi).
J. Soc. Glass Tech.	Journal of the Society of Glass Technology.
J. Tokyo Chem. Soc.	Journal of the Tokyo Chemical Society (now Journal of the Chemical Society of Japan).
J. Wash. Acad. Sci.	Journal of the Washington Academy of Sciences.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Paläontologie.
Jahrb. Min., Beil.-Bd.	Neues Jahrbuch für Mineralogie, Geologie und Paläontologie, Beilage-Band.
Jahrb. wiss. Bot.	Jahrbücher für wissenschaftliche Botanik.
Jap. J. Geol. Geog.	Japanese Journal of Geology and Geography.
Japanese J. Physics	Japanese Journal of Physics.
Jap. Med. Lit.	Japanese Medical Literature (discontinued in 1921).
K. Svenska Vetenskaps Akad. Handl.	Kongliga Svenska Vetenskaps Akademiens Handlingar.
Keram. i Steklo	Keramika i Steklo (Ceramics and Glass).
Lancet	The Lancet.
Latvij. Univ. Raksti	Latvijas Universitātes Raksti.

Abbreviated Title.	FULL TITLE.
Mem. Coll. Sci. Kyoto	Memoirs of the College of Science, Kyoto Imperial University.
Mem. R. Accad. d'Italia	Memorie della reale Accademia d'Italia.
Mem. Ryojun Coll. Eng.	Memoirs of the Ryojun College of Engineering.
Met. Ital.	Metallurgia Italiana.
Metall u. Erz	Metall und Erz.
Mikrochem.	Mikrochemie.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Missouri Agric. Exp. Sta. Res. Bull.	Missouri Agricultural Experiment Station Research Bulletins.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Mysore Univ. J.	The Half-yearly Journal of the Mysore University.
N. Z. J. Sci. Tech.	New Zealand Journal of Science and Technology.
Nach. Ges. Wiss. Göttingen.	Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen.
Naturwiss.	Die Naturwissenschaften.
Natuurwetensch. Tijds.	Natuurwetenschappelijk Tijdschrift.
Nebraska Agric. Expt. Sta. Bull.	Nebraska Agricultural Experiment Station Bulletin.
New Jersey Agric. Expt. Sta. Bull.	New Jersey Agricultural Experiment Station Bulletin.
Ohio Agric. Exp. Sta. Bull.	Ohio Agricultural Experiment Station Bulletins.
Pflanzenbau	Wissenschaftliches Archiv für Landwirtschaft. Abteilung A. Pflanzenbau.
Pharm. J.	Pharmaceutical Journal.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Pharm. Zentr.	Pharmazeutische Zentralhalle.
Pharm. Ztg.	Pharmazeutische Zeitung.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Physical Rev.	Physical Review.
Physikal. Z.	Physikalische Zeitschrift.
Planta	Zeitschrift für wissenschaftliche Biologie. Abteilung E. Planta. Archiv für wissenschaftliche Botanik.
Plant Physiol.	Plant Physiology.
Praktika	Praktika (Akademia Athenon).
Proc. Amer. Soc. Hort. Sci.	Proceedings of the American Society of Horticultural Science.
Proc. Austral. Inst. Min. Met.	Proceedings of the Australasian Institute of Mining and Metallurgy.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. Imp. Acad. Tokyo	Proceedings of the Imperial Academy of Japan.
Proc. III Int. Conf. Bit. Coal	Proceedings of the International Conference on Bituminous Coal: 3rd Conference.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam.
Proc. Nat. Acad. Sci.	Proceedings of the National Academy of Sciences.
Proc. Physical Soc.	Proceedings of the Physical Society of London.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Proc. Soc. Exp. Biol. Med.	Proceedings of the Society for Experimental Biology and Medicine.
Protoplasma	Internationale Zeitschrift für physikalische Chemie des Protoplasten.
Proc. World Eng. Congr. Tokyo	Proceedings of the World Engineering Congress, Tokyo, Japan.
Quart. J. Geol. Soc.	The Quarterly Journal of the Geological Society.
Quart. J. Pharm.	Quarterly Journal of Pharmacy and Pharmacology.

Abbreviated Title.	FULL TITLE.
Rec. Geol. Surv. India	Records of the Geological Survey of India.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Rensselaer Poly. Inst.	Rensselaer Polytechnic Institute, Engineering and Science Series.
Rev. Chim. pura appl.	Revista de Chimica pura e applicata.
Rev. Mod. Physics	Reviews of Modern Physics.
Rev. Sci. Instr.	Review of Scientific Instruments.
Rocz. Chem.	Roczniki Chemji organ Polskiego Towarzystwa Chemicznego.
Schweiz. Apoth.-Ztg.	Schweizerische Apotheker-Zeitung.
Sci. Papers Inst. Phys. Chem. Res. Tokyo	Scientific Papers of the Institute of Physical and Chemical Research, Tokyo.
Sci. Rep. Tôhoku Imp. Univ.	Scientific Reports, Tôhoku Imperial University.
Sitzungsber. preuss. Akad Wiss. Berlin	Sitzungsberichte der preussischen Akademie der Wissenschaften zu Berlin.
Soil Sci.	Soil Science.
Sucre. belge	La Sucrerie belge.
Suomen Kem.	Suomen Kemistilehte (Acta Chemica Fennica).
Svensk Kem. Tidskr.	Svensk Kemisk Tidskrift.
Tech. Rep. Tôhoku	The Technology Reports of the Tôhoku Imperial University.
Tidsskr. Kjemi Berg.	Tidsskrift for Kjemi og Bergvaesen.
Tonind.-Ztg.	Tonindustrie-Zeitung.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Ill. Acad. Sci.	Transactions of the Illinois State Academy of Science.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
Trans. Roy. Soc. S. Africa	Transactions of the Royal Society of South Africa.
Trans. State Inst. Test. Building Mat.	Transactions of the State Institute for Testing Building Materials and Glass.
Tsch. min. petr. Mitt.	Tschermaks mineralogische und petrographische Mitteilungen.
U.S. Bureau Mines Rep. Investigation	United States Bureau of Mines Reports of Investigations.
U.S. Dept. of Agric.	United States Department of Agriculture.
U.S. Geol. Survey Bull.	United States Geological Survey Bulletins.
Univ. Illinois Bull.	University of Illinois Bulletins.
Univ. Toronto Stud. Geol.	University of Toronto Studies: Geological Series.
Veröff. Kaiser Wilhelm-Inst. Silikatforsch.	Veröffentlichungen aus dem Kaiser Wilhelm-Institut für Silikatforschung in Berlin-Dahlem.
W. Austral. Geol. Surv. Bull.	Western Australia Geological Survey Bulletins.
Wiss. Arch. Landw.	Wissenschaftliches Archiv für Landwirtschaft.
Z. anal. Chem.	Zeitschrift für analytische Chemie.
Z. angew. Chem.	Zeitschrift für angewandte Chemie.
Z. anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie.
Z. deut. geol. Ges.	Zeitschrift der deutschen geologischen Gesellschaft.
Z. Elektrochem.	Zeitschrift für Elektrochemie (und angewandte physikalische Chemie).
Z. Krist.	Zeitschrift für Kristallographie.
Z. öffentl. Chem.	Zeitschrift für öffentliche Chemie (suspended in 1922).
Z. Pflanz. Düng.	Zeitschrift für Pflanzenernährung und Düngung.
Z. Physik	Zeitschrift für Physik.
Z. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Z. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Z. Unters. Lebensm.	Zeitschrift für Untersuchung der Lebensmittel.
Z. Vitaminforsch.	Zeitschrift für Vitaminforschung.
Zentr. Bakt. Par.	Zentralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.

ANNUAL REPORTS
ON THE
PROGRESS OF CHEMISTRY.

GENERAL AND PHYSICAL CHEMISTRY.

1. GENERAL.

IN spite of the aloofness of the atomic nucleus from ordinary chemical affairs, the problem of its structure [1] is in some ways the most fundamental one so far presented to chemistry. The great difficulty has been the absence of even the first beginnings of a theory about the forces holding the various components of the nucleus together. The radiations from radioactive substances, the displacement law, the identity of nuclear charge and atomic number, the existence of isotopes, and the production of protons by artificial disintegration, all go to show that protons, α-particles, and electrons are in some way involved in the make-up of the nucleus. That there is profound interaction of some kind between these components is revealed perhaps most strikingly by the mass defect. That there are sub-structures within the main structure is implied in all the theories in which the α-particles in the nucleus retain their identity. The existence of energy levels is strongly indicated by analysis of the γ-ray emissions. The size relationships of this extraordinary system are inconceivable in terms of macroscopic analogies, and most physical pictures which have been suggested inevitably contain inconsistencies and contradictions. Nevertheless, that some satisfactory form of nuclear statics and dynamics will presently be evolved seems almost certain. This anticipation is based upon the fact that in some respects nuclear processes, in spite of the difficulty of visualising them, are so very simple in their external results. One example may be quoted. The most striking experimental advance during the past year has been the artificial disintegration of elements by protons accelerated by extremely high voltages.[2] The lithium nucleus, when hit by a proton of several hundred thousand volts energy, appears to capture the proton and break up into two α-particles: $Li^7 + H^1 = 2He^4$. This opens up the prospect of a whole system of nuclear chemistry, by which theoretical predictions of stability relationships can be tested.

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[1] Cf. Discussion on Structure of Atomic Nuclei, *Proc. Roy. Soc.*, 1932, [*A*], **136**, 735; *A.*, 791.

[2] J. D. Cockcroft and E. T. S. Walton, *ibid.*, **137**, 229; *A.*, 893.

The Gamow theory,[3] treating the nucleus as a system containing α-particles confined within a high positive potential barrier through which they escape at a slow steady rate, enables a fairly accurate account to be given of the relation between the energy of α-particles and the half-life of the atoms emitting them. But if there are electrons as such in the nucleus, they would not be confined by this same kind of barrier: thus the picture is seen to be an incomplete one. F. A. Lindemann [1] has expressed the view that attempts to represent the nucleus in spatio-temporal terms cannot possibly succeed, or be more than metaphors.

W. Heisenberg [4] has recently started to construct a theory of the nucleus, which, while not spatio-temporal in the classical sense, is much more fundamental and direct than theories expressed in terms of potential barriers or other semi-empirical conceptions.

The great simplifying factor which has made Heisenberg's new theory possible is the discovery of the neutron.[5] This entity, which turns up when beryllium is bombarded with α-particles from polonium, appears to have unit mass and no charge. It could be conceived for some purposes as an electron and a proton fused together. The evidence that the beryllium radiation really does consist of neutrons is too detailed to be summarised briefly here, and the result will be accepted for the purpose of discussing the theory of nuclear forces.

If there are neutrons, it is no longer necessary to postulate the existence of free electrons in nuclei. The atomic weight has to be about twice the atomic number. Instead of interpreting this by saying that there are about twice as many protons as electrons we can now say that there are about equal numbers of protons and neutrons. According to Heisenberg, the best way is to regard the neutron, not as something containing a proton and an electron, but as an independent fundamental component of the nucleus. It is to be thought of, however, as capable of generating an electron and a proton in some way. The theory considers the forces between the various components of the nucleus. In the first place, there is the ordinary Coulomb repulsion between the protons, and, secondly, there are attractive forces between neutrons and between neutrons and protons. The attractive forces are treated quantum-mechanically. Those between neutrons and protons are of the "exchange" type.[6] (It may be well briefly to recall what this means. If a neutron and a proton are in proximity, and the negative charge changed places, passing into what was originally the proton, the final state would be indistinguishable from the initial. In wave mechanics the probability of a given state is determined by the amplitude of a certain function which varies harmonically with time. If two states are indistinguishable, the corresponding amplitudes wax and wane alternately at the expense of one another. This waxing and waning is analogous to the interchange of amplitude between two similar pendulums in resonance, and does indeed come about for the same mathematical reason, since it depends upon the identical frequencies associated with states of equal energies. Resonance is always associated with the production of a new frequency lower than the undisturbed frequency. Throughout quantum mechanics the connection between frequency and energy is of fundamental importance. Thus the same equations which predict the "interchange" of, say, the negative charge between the neutron and the proton, provide also for the existence of a state of lower energy than that corresponding to the energies of the completely separated particles. In other words, an attractive force exists.) The magnitude of the force is, in principle, derivable from "exchange integrals." Heisenberg constructs the Hamilton function for the nucleus, and from considerations of a rather general character arrives at a number of interesting results. Considering the influence of the exchange forces only, he concludes that the minimum energy, *i.e.*, maximum stability, would be reached when the numbers of neutrons and protons present are about equal. The influence of the other forces is to displace the stable number somewhat in favour of neutrons.

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[3] Cf. *Ann. Reports*, 1930, **27**, 26.

[4] *Z. Physik*, 1932, **77**, 1; **78**, 156; *A.*, 894, 1074.

[5] J. Chadwick, *Proc. Roy. Soc.*, 1932, [*A*], **136**, 692; *A.*, 790; (Mme.) I. Curie and F. Joliot, *Nature*, 1932, **130**, 57; *A.*, 895.

From the known stability of helium nuclei, it must be supposed that a system of two protons and two neutrons forms something analogous to a "closed" or "completed shell." The picture of β-ray disintegration is as follows: a nucleus consisting only of neutrons would change neutrons into protons by sending out β-rays until the energy which is gained by adding a proton is exactly equal to that which is used up in removing a neutron. For smaller numbers of neutrons the nucleus is stable towards β-disintegration. If the number of neutrons gets too small, the Coulomb repulsion of the positive charges leads to α-ray decay: α-particles, and not protons, are emitted, since β-disintegration ceases at a point where the removal of a proton still requires energy, though an α-particle, being less tightly bound than a proton, can escape. The ratio, n_1/n_2, of the number of neutrons to protons has, for a given value of n_2, an upper and a lower limit, corresponding to β- and α-disintegration respectively. Owing to the great stability of the helium nucleus, there are often two successive β-ray changes if initially the atomic number is even, but if one starts from an odd atomic number, there may only be one. β-Ray changes may be followed by α-disintegration until n_1/n_2 once again rises above a limiting value.

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[6] Cf. *Ann. Reports*, 1930, **27**, 14.

Heisenberg investigates the stability of nuclei with even and odd numbers of neutrons, and also deals with the question of the scattering of γ-rays by atomic nuclei.

In the last Report, reference was made to the view that the emission of γ-rays is associated with the transition of α-particles between energy levels in the nucleus. Further work lends additional support to this idea. It has been shown, for example, that certain γ-rays, known to be associated in some way with thorium-*C* or thorium-*C′*, are given out as an immediate consequence of the disintegration of thorium-*C*.[7] Again, actinium emanation emits two groups of α-particles : in the transformation of the emanation into actinium-*A*, γ-rays are emitted, the quantum energy of which is found to be of the right order of magnitude to correspond to the difference in energy of the two α-particle groups.[8]

Perhaps one of the most striking results of quantum mechanics is the prediction of enhanced probability of transition between two states of a complex system when the total energy of one state is very nearly equal to that of the other. (The phenomenon is called resonance, since it depends mathematically upon equality of frequency in the wave functions describing the different states.) From the general point of view, therefore, great interest attaches to the interpretation given by J. Chadwick and J. E. R. Constable[9] to their experiments on the artificial disintegration of fluorine and aluminium nuclei by α-particles. When these elements are bombarded with α-particles from polonium, the protons liberated can apparently be resolved into definite groups. (These groups, moreover, occur in pairs, suggesting that there are two ways in which an α-particle can be captured, the first giving an excited nucleus and a short-range proton, the second giving a stable nucleus and a long-range proton.) The four groups of two found with aluminium are supposed to indicate the existence in the nucleus of four "resonance levels." Penetration of the nucleus by the α-particle with insufficient energy to surmount the "potential barrier" can occur if the particle has exactly the energy corresponding to a resonance level. A detailed consideration of the technique of the kind of experiment upon which these conclusions are based is obviously far outside the scope of this Report. It ought, however, to be mentioned that in certain cases difficulties of interpretation seem to arise.[10] This means that, while the theoretical interest of the problems raised is very great, even more investigation is necessary before the fullest confidence can be felt in any general conclusion.

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[7] C. D. Ellis, *Proc. Roy. Soc.*, 1932, [*A*], **136**, 396.

[8] (Lord) Rutherford and B. V. Bowden, *ibid.*, p. 407.

[9] *Ibid.*, **135**, 48 ; *A.*, 318.

Another line of attack on the nucleus which looks like being successful is the investigation of nuclear magnetic moments and what are called "$g(I)$ factors," *i.e.*, ratio of magnetic to mechanical moment, based upon the measurement of the hyperfine structure of spectral lines.[11] This is just mentioned here, but it is not proposed to discuss the results in detail.

It will be evident, even from the few examples quoted above, that nuclear chemistry is in a state of rapid development.

We will now turn to the consideration of certain matters connected with the more accessible parts of the atom, starting with some recent work on the nature of the chemical bond.

The customary distinction between an ionic bond and a covalent or electron-pair bond appears to be quite sharp and definite as long as attention is fixed upon extreme cases. But the question whether there is a continuous transition from one to the other has always been a subject for discussion. From a "semi-quantitative" quantum-mechanical treatment of the problem, L. Pauling[12] arrives at the conclusion that there will be a continuous transition from one type of bond to the other only when the lowest ionic state of the molecule and the lowest covalent state have the same number of unpaired electrons. Making approximate estimates of different kinds of binding energies, he concludes that alkali halides are ionic, that the molecules HCl, HBr, and HI have electron-pair bonds, while HF is "largely ionic."

When two electronic structures of about the same energy are possible for a molecule, the quantum-mechanical resonance phenomenon comes into play with rather strange results. The wave function for the normal state of the system is best represented not by either of the functions describing the two separate states but by a linear combination of the two functions. The meaning of this is supposed to be that the molecule oscillates rapidly between the two possible structures. Carbon monoxide, according to Pauling, provides an example of this kind of behaviour and fluctuates between the structures given by $:C::\ddot{O}:$ and $:C:::O:$, the latter being the predominant form.[13]

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[10] Cf. discussion at the end of the paper by E. Steudel, *Z. Physik*, 1932, **77**, 139; *A.*, 980.

[11] Cf. J. C. McLennan, *Proc. Roy. Soc.*, 1932, [*A*], **136**, 735; *A.*, 791.

[12] *J. Amer. Chem. Soc.*, 1932, **54**, 988; *A.*, 561.

It is a striking fact that the energies of individual bonds as derived from heats of formation and heats of combustion are approximately constant.[14] The quantum-mechanical translation of this fact may be expressed by saying that the properties of a bond are often "determined by one single-electron orbital wave function for each atom and are not strongly affected by other atoms in the molecule." To what extent this principle can be established rigidly by *a priori* reasoning the reviewer is not competent to state. But even if largely empirical, the rule is a useful one. Pauling[15] concludes from an examination of thermochemical evidence that the energies of normal covalent bonds are additive. This means that relations of the following kind hold: $A{:}B = \frac{1}{2}(A{:}A + B{:}B)$, where A:B represents the energy of a bond between A and B.

This applies only to normal covalent bonds, by which are meant bonds in which the electrons are equally shared by the two atoms. If A and B are not equally electronegative the bond assumes a certain ionic character. According to Pauling, the energy of an actual bond must be at least as great as that for a normal covalent bond. Moreover, the difference between the actual energy and that calculated by assuming additive relationships will be greater the more pronounced the ionic character of the bond. For example, H:H is 4·44 v.e., F:F is 2·80; both of these are normal bonds, since the two atoms are in each case identical. From the additive principle, the normal covalent bond between H and F should have an energy $\frac{1}{2}(4{\cdot}44 + 2{\cdot}80) = 3{\cdot}62$. The actual value for H:F is 6·39, which is in fact much greater than the "normal" value. The difference, Δ, decreases steadily as we pass to the heavier halogens: with H:I the value calculated from additivity is 2·99, while the real value is 3·07, giving $\Delta = 0{\cdot}08$. Pauling finds Δ to be positive in 20 out of 21 examples. It then appears that there are regularities among the Δ values themselves: the values of $\Delta^{1/2}$ are observed to be approximately additive. This relation is illustrated by the following numbers, the unit being the electron-volt.

C–H actual	4·34	C–F actual	5·40
C–H from additive relation	4·02	C–F from additive relation	3·20
Δ	0·32	Δ	2·20
$\Delta^{1/2}$	0·57	$\Delta^{1/2}$	1·48

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[13] See (12); also *Proc. Nat. Acad. Sci.*, 1932, **18**, 293; *A.*, 562.

[14] Cf. *Ann. Reports*, 1931, **28**, 385.

[15] *J. Amer. Chem. Soc.*, 1932, **54**, 3570; L. Pauling and D. M. Yost, *Proc. Nat. Acad. Sci.*, 1932, **18**, 414; *A.*, 901.

Thus $\Delta^{1/2}_{H-C} + \Delta^{1/2}_{C-F} = 2{\cdot}05$. Similarly from N–H and N–F it is found that $\Delta^{1/2}_{H-N} + \Delta^{1/2}_{N-F} = 2{\cdot}06$.

This suggests that the actual value of any Δ_{AB} can be expressed in the form $(x_A - x_B)^2$, where x_A and x_B are co-ordinates of the elements in some scale. Thus if the following numbers are assigned to various elements :

H	P	I	S	C	Br	Cl	N	O	F
0·0	0·10	0·40	0·43	0·55	0·75	0·94	0·95	1·40	2·00

the value of any Δ_{AB} can be calculated. For example,

Δ_{C-H} will be $(0{\cdot}55 - 0)^2 = 0{\cdot}55^2$,
Δ_{C-F} will be $(2{\cdot}00 - 0{\cdot}55)^2 = 1{\cdot}45^2$, and so on.

Since the magnitude of Δ_{AB} depends upon the ionic character which the bond acquires by the unequal sharing of electrons between the two atoms, the greater its value the further apart in a scale of electronegativity must the two atoms be. Thus the above series gives a quantitative measure of the electronegative character of the different atoms. The arrangement of the atoms in this definite order is extremely useful for purposes of discussing the properties and reactions of chemical substances. Quite often the relative degrees of electronegativeness of various atoms have had to be assumed *ad hoc* for the purposes of this or that theory, but the present series provides a standard based upon independent measurements. Incidentally, the series is useful for computing bond energies which are not easily accessible to measurement.

The forces which atoms exert upon one another are not of a simple nature. The Heitler–London type of valency force, which gives rise to a bond consisting of two electrons with antiparallel spin moments, is reinforced or opposed by various other interactions including " polarisation forces." If two atoms with parallel spin moments approach, the effect predicted by the Heitler–London treatment is repulsion. This is opposed by the attractive force due to mutual polarisation. For two hydrogen atoms the influence of this factor is considered to be unimportant, but with the alkali metals it seems that the energy relations are quite different and that " polarisation molecules " may be formed. According to H. Kuhn,[16] there occur in alkali-metal vapours, near the principal series lines, absorption bands due to such molecules. The bands are said to be quite different from the well-known bands of the Na_2 type, and occupy a very narrow spectral region near the atomic lines, on account of the smallness of the energy of dissociation. Kuhn suggests that the following sequence should be traversed by alkali absorption spectra as the pressure is increased : atomic, true molecules (singlet state), polarisation molecules, and finally, continuous absorption from atoms at the moment of collision—“ quasi-molecules.” What is interesting from our present point of view is not the validity of any given interpretation of particular spectroscopic observations, but the elaborate possibilities of atomic interaction which appear in general to be possible.

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[16] *Z. Physik*, 1932, **76**, 782.

We now advance one stage further in complexity, namely, to carbon compounds.

The success with which organic chemistry has solved its problems by the aid of its own conceptions about the nature of chemical bonds has, during the last few years, stimulated theoretical physicists to attempt the translation of these conceptions into the language of quantum mechanics. It is as well to realise at the outset that even the simplest problems of organic chemistry are much too complicated for anything like a complete and fundamental treatment not based upon drastic simplification and not introducing a considerable measure of assumption. The theoretical investigation, therefore, can hardly be expected to predict new phenomena in organic chemistry. Nevertheless, it is satisfactory that the known phenomena can be described in terms acceptable to physicists, and that the rules can be formulated in ways which at least are not inconsistent with quantum-mechanical principles. In previous Reports reference has been made to theoretical interpretations of the rigidity of double bonds, the stability of ring systems, and substitution into the benzene nucleus.[17] Such matters have been further dealt with by F. Hund,[18] and by E. Hückel,[19] and H. Eyring [20] has discussed the problem of steric hindrance.

Hückel refers the characteristic behaviour of benzene to the existence of a kind of closed group of six $[p]_h$ electrons (the proper function of which has a node in the plane of the ring). He treats their interaction by a method similar to that used by Bloch for working out the interaction of electrons in metals, and extends the discussion to include naphthalene, anthracene, phenanthrene, diphenyl, and conjugated chain systems. All the rings are assumed to be plane, the plane arrangements being “ stabilised by the charge distribution of the $[p]_h$ electrons with the node of the proper functions in the plane of the atoms.” He makes calculations about the symmetry of the various proper functions, and arrives at various conclusions. Condensed ring systems all possess completed electron groups like benzene, and the binding energy per electron is not very different from that of the electrons in benzene. Hückel remarks that the addition of alkali metals occurs with different ease with the different compounds, and that the "same order exists for the energy of the lowest unoccupied states." The position of the lowest unoccupied state (*i.e.*, its energy level) is a measure of the "Abgeschlossenheit" (*i.e.*, completeness, closed nature, or stability) of the electron group in respect to the taking up of electrons.

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[17] Hückel's views on this matter have been criticised by A. Lapworth and R. Robinson, *Nature*, 1932, **129**, 278.

[18] *Z. Physik*, 1932, **73**, 565; *A.*, 215.

[19] *Ibid.*, **76**, 628.

[20] *J. Amer. Chem. Soc.*, 1932, **54**, 3191; *A.*, 996.

Eyring's discussion of steric hindrance is based upon different principles. He uses potential-energy curves first in considering the approach and "collision" of two molecules, and then in treating the rotation of two methyl groups about an axis joining the two carbon atoms.

The transition between covalent and electrovalent bonds, and the complexity of atomic interactions in general, are subjects which come very much into prominence in the theory of electrolytes. The Debye–Hückel theory having shown that the most important properties of dilute solutions of strong electrolytes can be accounted for by assuming complete ionisation, the question arises whether existing deviations from the theory are partly due to the existence in solution of real molecules even of such substances as sodium chloride. This matter, and also the question of heat of dilution, which depends upon interionic forces and the forces between ions and dipole solvent molecules, is discussed in the following sections.

C. N. H.

2. THE "TRUE" DEGREE OF DISSOCIATION OF STRONG ELECTROLYTES.

This problem presents itself in several rather complicated aspects. In the first place it involves the prior question as to whether anything equivalent to a molecule really exists in the solution of a strong electrolyte; if this question be decided in the negative, it is still legitimate to enquire whether it is not desirable on the grounds of expediency alone to treat as molecules complexes of oppositely charged ions associated with a certain degree of permanence, and thus somewhat arbitrarily to divide the solution into ions and molecules. The second major problem, which arises if either of the first two questions is answered in the affirmative, is that of determining the "true" degree of dissociation.

The answer to the first question—whether molecules exist in solutions of strong electrolytes or not—may be sought in two distinct ways. On the one hand, we may examine the electrolyte for properties which we have reason to believe are characteristic of undissociated molecules; this is the more distinctively experimental approach. On the other hand, we may endeavour to refine the original calculations of Debye and Hückel so as to extend their applicability to less dilute solutions; if the mathematical difficulties involved in this can be overcome, we can then compare the theoretical predictions with the experimental data and thus test the adequacy of the purely electrostatic picture of a moderately concentrated solution.

The only properties characteristic of undissociated molecules, which are available in this connexion, are their volatility or solubility in a non-polar solvent and their optical properties. The vapour pressure of hydrogen halides above their aqueous solutions is unmistakable qualitative evidence of the existence of a small concentration of molecules in solution, but no quantitative estimate of their amount can be made without introducing a hypothetical partition coefficient for the molecules. By using arguments by analogy with alkyl halides or with hydrogen cyanide, respectively, the concentration of molecules in 0·01M-hydrogen chloride solution was found to be $5{\cdot}9 \times 10^{-12}$ by L. Ebert[21] and 3×10^{-10} by K. Fajans.[22] Treating the vapour pressure data in a different way, W. F. K. Wynne-Jones[23] has estimated the concentration of undissociated hydrogen chloride in M-solution to be 4×10^{-8}. These values are probably of the right order and indicate the extremely low concentration of molecules present at a concentration where the conductivity ratio is about 0·97. Partition methods are inapplicable to salts, and here we have to rely on the optical properties peculiar to undissociated molecules; these are respectively the refractive index, the absorption spectra, and the Raman spectra of electrolytic solutions. Independently of his rather speculative theory of deformable ions, K. Fajans[24] has shown that the change of the refraction of salt solutions with increasing concentration runs parallel with the changes in refraction with concentration of the corresponding acids where the refraction is tending towards the refraction of the pure covalent acid; this may be regarded as qualitative evidence of incomplete dissociation. Fajans's other more quantitative arguments to the same end are based on his hypothesis of deformable ions and are more equivocal. E. Schreiner[25] has endeavoured to make a quantitative estimate of the degree of dissociation of hydrogen chloride and bromide in 4N-solution from refraction data; his values, 94·6% and 96·6% respectively, correspond to much less complete dissociation than the partition data suggest.

[21] *Naturwiss.*, 1925, **13**, 393.
[22] *Trans. Faraday Soc.*, 1927, **23**, 357; *A.*, 1927, 1023.
[23] *J.*, 1930, 1064; *A.*, 1930, 859.
[24] See E. Lange, *Physikal. Z.*, 1928, **29**, 767.
[25] *Naturwiss.*, 1925, **13**, 245.

The absorption curves of nitric acid and of various salts over a range of concentrations show a common intersection point, according to H. von Halban.[26] Such a phenomenon would occur if the solute were changing progressively from one form with its characteristic absorption curve into another. Halban regards the two forms as molecules and ions respectively; he finds further evidence for incomplete dissociation in the deviations from Beer's law shown by numerous salts in concentrated solution.

Of the experimental methods available for the detection of undissociated molecules in solution, there can be little doubt that the study of the Raman spectra of electrolytes is by far the most elegant and the most satisfactory from a theoretical point of view. The interatomic linkage formed when two ions unite to form a molecule must lead to the development of one or more distinctive Raman lines. If, therefore, the Raman spectrum of a solution of an electrolyte shows lines other than those known to be characteristic of the solvent and of the constituent ions of the electrolyte, it may be safely inferred that undissociated molecules are present;[27] since ions whose electron shells are of the inert-gas type produce no Raman lines themselves, the criterion is peculiarly clear-cut for salts like the alkali halides. The principal defect of the method is that, at the present state of development of technique, the line-producing molecule must be present in substantial concentration if it is to be detected; Raman spectra cannot therefore be expected to show the presence of undissociated molecules whose concentration is much less than, say, $0{\cdot}1N$. The experimental results of L. A. Woodward [28] and others reveal no molecules as present in aqueous solutions of potassium chloride, hydrogen chloride, potassium cyanide, hydrogen fluoride, iodic acid, and sodium hydroxide amongst others, whereas solutions of nitric acid, mercuric chloride, and mercuric cyanide show molecules; the Raman spectra of solutions of sulphuric acid show very clearly the progressive disappearance of the molecules and intermediate ions as the concentration diminishes. Perhaps the only surprising feature of the results is the absence of any evidence for molecules in solutions of hydrogen fluoride.

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[26] *Z. Elektrochem.*, 1928, **34**, 489.

[27] Except for the theoretical possibility that the mutual approach of the ions in concentrated solution may remove the " Verbot " on an existing frequency inside one of the ions by disturbing the symmetry property which previously forbade its appearance; see G. Placzek, *Z. Physik*, 1931, **70**, 84; *A.*, 1931, 893, and Leipziger Vorträge (" Molekülstruktur "), 1931, p. 71. (Private communication from Mr. L. A. Woodward.)

[28] *Physikal. Z.*, 1931, **32**, 777; *A.*, 1931, 1367. This paper contains a useful bibliography.

Summarising the evidence derived from the study of properties believed to be characteristic of undissociated molecules, one may say that, apart from the acids, there is virtually no unequivocal evidence of the existence of molecules in solution of " strong " uni-univalent electrolytes at any concentration.

The more noteworthy of the attempts to extend the range of validity of the ionic-atmosphere calculations to less dilute solutions, while preserving the principle of complete dissociation, are the so-called " second approximation " of P. Debye and E. Hückel [29] and the treatment of T. H. Gronwall, V. K. LaMer, and K. Sandved.[30] The former of these replaces the point charges of the simple theory by spheres of finite size with a least distance of approach a. The introduction of this parameter into the expression for the logarithm of the activity coefficient has the effect of increasing the activity coefficient to an extent which increases with the size of a; that is to say, with ions of finite size the activity coefficient diminishes less rapidly with increasing concentration than is predicted for point-charge ions. Quantitatively this " second approximation " is capable of expressing the experimental activity coefficients for electrolytes with *large ions* up to concentrations of the order of $0{\cdot}1N$, using quite plausible values for a; on the other hand, for some electrolytes, such as potassium nitrate and potassium iodate, the expression leads to impossibly small values for a. Thus the single auxiliary assumption of a finite size for the ions is seen to be inadequate to account for the facts in more concentrated solution.

A more thorough and more complicated extension of the simple theory is that of Gronwall, LaMer, and Sandved. Their treatment not only introduces the least distance of approach, but also takes into account the further terms of the series for the potential energy of the ion due to the atmosphere, a series of which the simplified treatment neglects all but the first term. The notable features of the resulting equation for the logarithm of the activity coefficient are that, for small ionic radii, activity coefficients less than those of the simplified theory are predicted, and also that the behaviour of electrolytes like potassium nitrate and potassium iodate is adequately represented up to $0{\cdot}1N$-concentrations by postulating small but not impossible values for a.

Thus, so far as activity coefficients are concerned, the treatment of these authors gives an adequate representation of the facts up to $0{\cdot}1N$-solutions with the aid of an admittedly complicated equation, which, however, contains only one adjustable parameter a, whose values are always physically plausible. When the same treatment is extended to heats of dilution, as has been done by E. Lange and J. Meixner,[31] it is, however, found to be inadequate to explain the facts, and, in particular, the a values necessary to account for the heats of dilution of a series of salts are sometimes graded in magnitude in the opposite sense to the values necessary to make the activity coefficients " fit."

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[29] *Physikal. Z.*, 1923, **24**, 185; *A.*, 1923, ii, 459.

[30] *Ibid.*, 1928, **29**, 358; *A.*, 1928, 841.

Although neither the " second approximation " of Debye and Hückel nor the treatment of Gronwall, LaMer and Sandved (nor several other attempts in the same direction) has succeeded in accounting for the behaviour of electrolytes outside the limiting range of concentration in purely electrical terms, the conclusion must certainly not be drawn that the postulation of undissociated molecules is therefore necessary at these concentrations. The fact of the matter is that the difficulties of any complete treatment of the electrical forces in concentrated solutions are beyond our mathematical equipment at the present time. The attempts just described were only made possible by concentrating on one or two of the complicating factors and neglecting the remainder. Apart from such factors as the influence of the electrolyte on the dielectric constant of the solvent and the temperature variation of a, the proximity of the ions in concentrated solution must certainly add to the long-range Coulomb forces between the ions the far from negligible short-range forces generally characterised as " van der Waals forces." Pending an adequate mathematical treatment of the problem, there is some justification for regarding the postulation of undissociated molecules in such solutions as an unnecessary hypothesis.

Mid-way between the purely electrostatic picture of a solution and the view which assumes the existence of undissociated molecules is the " ion-association " theory of N. Bjerrum.[32] He points out that the Debye–Hückel postulate, that the potential energy of an ion is much less than its kinetic energy, is less likely to be true the higher the valency of the ions, the lower the dielectric constant of the solvent, and the closer the ions can approach one another (*i.e., the smaller their radii*). He shows that the probability of a z-valent ion being at a distance r from a similar ion of opposite sign passes through a minimum value given by the equation

$$r_{\text{min.}} = \varepsilon^2 z^2 / 2DkT$$

where ε is the electronic charge, D the dielectric constant of the solvent, k the Boltzmann gas constant, and T the absolute temperature. Inside this radius the probability increases very rapidly owing to the strong attractive forces exerted between the ions.

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[31] *Physikal. Z.*, 1929, **30**, 670; *A.*, 1928, 1389.

[32] *Ergebnisse d. exakt. Naturwiss.*, 1926, **5**, 125.

For aqueous solutions of uni-univalent electrolytes at 18°, $r_{\text{min.}}$ has the value 3·52 Å. An electrolyte with ions the sum of whose radii is greater than this critical value, is treated by Bjerrum as completely dissociated and susceptible to the unmodified Debye–Hückel treatment. If the sum of the ionic radii is less than $r_{\text{min.}}$, Bjerrum arbitrarily divides the ions into two groups, namely, those whose distance apart is more than $r_{\text{min.}}$, which are assumed to be free, and those within the minimum distance, which he treats as "ion-pairs." The proportion of ion-pairs is calculated by integrating the probability function over the interval from $r_{\text{min.}}$ down to the sum of the ionic radii.

Although the line of demarcation between free and associated ions is thus drawn at a quite arbitrary point (the probability minimum being associated with no physical discontinuity) Bjerrum applies the mass-action law to the equilibrium between ion-pairs and free ions. The activity coefficient of the ion-pairs is put equal to unity and that of the free ions is calculated from the Debye–Hückel "second approximation," $r_{\text{min.}}$ being put in as the a parameter. In this way a series of degrees of "ion-association" are calculated which increase with concentration and also with diminution in the radii of the ions concerned. The over-all activity coefficients may then be calculated and are found to be in good agreement with experiment up to concentrations of the order of 0·1N. Like the expression of Gronwall, LaMer, and Sandved (and in contrast to the "second approximation" of Debye and Hückel), Bjerrum's treatment leads to values of the ionic radii which are always positive and of plausible magnitude.

In spite of its somewhat arbitrary mathematical derivation, the hypothesis of "ion-association" has various attractive features. It represents the experimental facts as adequately as the more complete mathematical analyses; it gives a clearer physical picture of the solution; and it is perhaps worth noting that the possibility of "ion-complexes" (composed of more than two ions) at high concentrations in solvents of low dielectric constant offers a possible explanation of the increase of equivalent conductivity at high concentrations after passing through a minimum as observed by Walden.

The "ion-association" hypothesis can hardly be said to be one of complete dissociation, since the ion-pairs of Bjerrum are regarded as temporary juxtapositions of undeformed and completely solvated ions whose equilibrium with "free" ions is for reasons of expediency treated as subject to the mass-action law. There remain to be considered two points of view in both of which is postulated an equilibrium of the true Arrhenius type (corrected for activity coefficients) between undissociated molecules and ions subject to the electrostatic forces of the Debye–Hückel limiting equations. The first of these is primarily associated with the name of W. Nernst and is based on a consideration of heats of dilution; the second, due to C. W. Davies and to L. Onsager in the first instance, is based on conductivity data.

Nernst [33] divides the experimentally observed integral heat of dilution into two parts; the first of these is the heat absorbed in the dissociation of the un-ionised portion of the electrolyte, and the second is the electrostatic heat of dilution of the ionised portion. This leads to the equation

$$V_c = -Q(1 - \alpha) + B\alpha\sqrt{\alpha c}$$

where Q is the heat of ionisation of the molecules, c the concentration of the solution, α the true degree of dissociation, and B the numerical coefficient of the electrostatic heat of dilution (see equation 3; p. 30). The validity of the mass-action law for the dissociation of the ions being assumed, it is possible by applying the van 't Hoff isochore to the measurements of the heat of dilution of an electrolyte at two temperatures to evaluate the two unknowns Q and α by a series of successive approximations, and thus to predict the variation of the integral heat of dilution over the whole range of concentrations. Several approximations and assumptions are employed; instead of the theoretical proportionality factor between electrostatic heat of dilution and the square root of the concentration, Nernst equates B to the observed slope for lithium chloride which is thus regarded as an ideal completely dissociated electrolyte; furthermore, the activity coefficient of the ions is equated to unity over the complete concentration range; finally, it is assumed that the electrostatic contribution to the heat of dilution maintains its linear relation with the square root of the concentration up to the highest concentrations involved. In spite of these simplifying assumptions, it is found that the Nernst equation represents the experimentally determined heats of dilution satisfactorily up to concentrations of the order of $N/3$ and N. The degrees of dissociation of sodium chloride and potassium nitrate in $0{\cdot}1N$-solution are given as 98·9% and 95·2% respectively at 18°. In spite of its concordance with experimental facts for the uni-univalent salts studied, the Nernst treatment cannot be regarded as entirely satisfactory since it embodies several assumptions that are certainly untrue; it is also at variance with the individualities in the heats of dilution of electrolytes (referred to on p. 32) at very low concentrations where the undissociated portion, which is roughly proportional to the first power of the concentration, can no longer be of significance. A recent paper by E. Plake,[34] in which the heats of dilution of uni-bivalent and bi-bivalent electrolytes are treated from the Nernst point of view, arrives at the conclusion that, whereas uni-univalent electrolytes are incompletely dissociated, the electrolytes of higher valency are completely dissociated; this inference is so much at variance with accepted views that it can hardly fail to shake one's confidence in the underlying hypothesis.

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[33] *Z. Elektrochem.*, 1927, **33**, 428; *A.*, 1928, 127.

The derivation of true degrees of dissociation from conductivity measurements has been treated by L. Onsager,[35] C. W. Davies,[36] M. Wien,[37] and other workers: their respective treatments are identical in principle although the most accurate method is probably that of Davies, which may be taken as representative of the others. The fall of equivalent conductivity with increasing concentration is attributed jointly to (1) the decrease in mobility due to electrostatic forces as calculated by the Debye–Hückel–Onsager equation and (2) the diminution in number of the ions free to conduct owing to the formation of undissociated molecules. Since the first effect is readily calculable, the magnitude of the second can be found.

The method of calculation employed by Davies is as follows: Let α be the true degree of dissociation of an electrolyte, whose limiting equivalent conductivity is Λ_0, at a concentration where the equivalent conductivity is Λ_c. Then α is not given by Λ_c/Λ_0 but by Λ_c/Λ_x, where Λ_x is the sum of the ionic mobilities in the solution considered. Since the concentration of the ions is $c\Lambda_c/\Lambda_x$, the value of Λ_x is given by the Onsager equation, which for an aqueous solution of a uni-univalent electrolyte at 25° is

$$\Lambda_x = \Lambda_0 - (0{\cdot}227\Lambda_0 + 59{\cdot}78)\sqrt{c\Lambda_c/\Lambda_x}$$

This is a cubic equation in Λ_x and is solved as such by Wien; Davies prefers to evaluate Λ_x by a short series of successive approximations.

When Λ_x has been determined in this way, the true degree of dissociation is immediately evaluated as Λ_c/Λ_x. Davies then applies the mass-action law, corrected for the activity coefficients of the ions, to the true concentrations of ions c_i and undissociated molecules c_u obtained in this way, and writes

$$c_i^2 f_i^2/c_u = K$$

the activity of the undissociated molecules being put equal to unity. The constancy of this relation can be tested directly or graphically in the following manner: At high dilutions $-\log f_i = A\sqrt{c_i}$; taking logarithms, we may therefore write the above equation as

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[34] *Z. physikal. Chem.*, 1932, [*A*], **162**, 257.

[35] *Physikal. Z.*, 1927, **28**, 277; *A.*, 1927, 517.

[36] *Trans. Faraday Soc.*, 1927, **23**, 351.

[37] See H. Falkenhagen, "Elektrolyten," p. 299.

$$\log c_i^2/c_u = \log K + 2A\sqrt{c_i}$$

Plotting $\log c_i^2/c_u$ against $\sqrt{c_i}$, we should therefore expect to get a straight line whose slope is $2A$ and whose intercept on the axis of zero concentration is $\log K$.

Davies has evaluated the true degrees of dissociation of a number of salts in this way, and has obtained corrected mass-action constants which are a very marked improvement on the Ostwald " constants " for the same electrolytes. Its extension to non-aqueous solutions, where incomplete dissociation is much more common, is likely to be of great value; unfortunately, its application is there handicapped by the scarcity of reliable values for Λ_0 and by the very small concentration range over which Onsager's equation is valid in solvents of low dielectric constant. Although the validity of this method of determining true degrees of dissociation can only be tested over the range of concentrations in which Onsager's equation is applicable, it is important to notice that, provided that a satisfactory constant can be evaluated for a given electrolyte over this range, the degree of dissociation can then be found at higher concentrations from measurements of activity alone. The only limit to such an extension is imposed by the condition that the activity of the undissociated molecules must approximate to the concentration. It is unfortunate that the method does not lend itself to cases where dissociation must be very nearly complete; the mode of calculation is susceptible to considerable error unless the un-ionised fraction is present in appreciable amounts. Thus, in the case of nearly all uni-univalent salts in water, the un-ionised fraction only becomes measurable at concentrations where the Onsager equation is inapplicable, and recourse must be had to an empirical conductivity equation embodying a viscosity correction. Notwithstanding these limitations and the fact that no physical picture is afforded of the nature of the " undissociated " portion of the electrolyte, the Davies method of treating conductivity data is probably the least equivocal way of gaining information as to the degree of dissociation of electrolytes.

J. H. W.

3. The Thermochemistry of Electrolytes.

At the time when the thermochemistry of electrolytes was last touched on in these Reports,[38] it was necessary to record a serious discrepancy between the predictions of the interionic attraction theory concerning the heat of dilution of electrolytes and the experimental data available at the time. Theory predicted that the heat of dilution of the ideal electrolyte in aqueous solutions must be positive, whereas the measurements then published showed negative heats of dilution for the majority of electrolytes. Precise measurements of heats of dilution of electrolytes at very low concentrations carried out over the last five years by E. Lange[39] and his collaborators have served to remove this discrepancy and to confirm in a general way the interionic attraction theory in this field.

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[38] *Ann. Reports*, 1927, **24**, 23.

The heat evolved when a volume of solution sufficient to contain one mol. of electrolyte is diluted to infinite dilution is called the integral heat of dilution and is usually denoted by the symbol V_c. In the ideal electrolyte of the Debye–Hückel theory this heat effect is due to purely electrostatic forces, and its magnitude may be calculated by the application of the Gibbs–Helmholtz equation to the electrical free energy of the solution. We thus have

$$Q_c = F_e - T(\partial F_e/\partial T)_v \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where Q_c is the heat of dilution per c.c., and F_e, the electrical free energy per c.c. of the solution, is negative for all finite concentrations of the ideal electrolyte and converges to zero as the concentration becomes infinitely small. The solution of this equation for a binary electrolyte consisting of two z-valent ions leads to the expression[40]

$$V_c = -\frac{N\varepsilon^2 z^2}{D}\sqrt{\frac{8\pi z^2\varepsilon^2 N}{1000DkT}}\left(1 + \frac{T}{D}\cdot\frac{dD}{dT}\right)\sqrt{c} \quad . \quad . \quad . \quad (2)$$

where N = Avogadro number,
ε = electronic charge,
k = Boltzmann gas constant,
D = dielectric constant of the solvent,
and c = concentration of the solution in mols./litre.

Giving the universal constants their numerical values, inserting the dielectric constant of water and its temperature coefficient, and converting from ergs to calories, we obtain the expression for aqueous solutions at 25° :

$$V_c = +\ 490z^3\sqrt{c} \text{ calories} \quad . \quad . \quad . \quad . \quad (3)$$

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[39] Thirty-six papers have already appeared, of which the last is by H. Hammerschmid and E. Lange, *Z. physikal. Chem.*, 1932, [*A*], **160**, 445; *A.*, 913. For summarising paper, see E. Lange and A. L. Robinson, *Chem. Reviews*, 1931, **9**, 89.

[40] O. Gatty (*Phil. Mag.*, 1931, **11**, 1082; *A.*, 1931, 685) and, later but independently, G. Scatchard (*J. Amer. Chem. Soc.*, 1931, **53**, 2037; *A.*, 1931, 913) have pointed out that this equation involves the erroneous assumption that $(dD/dT)_v$ and $(dD/dT)_p$ are mutually interchangeable. The corrected equation includes an extra term involving the thermal expansion of the solvent; this term is small for water but of significance in non-aqueous solvents.

The important features of this expression are (1) that the heat of dilution (or more precisely the electrostatic contribution to the heat of dilution) is always positive in aqueous solutions—this is equally true for virtually all solvents of high dielectric constant (see below);

(2) that the heat of dilution is proportional to the square root of the concentration;

(3) that the heat of dilution is identical for electrolytes of the same valency type.

The positive sign of the electrostatic contribution to the heat of dilution is remarkable. It seems at first sight unreasonable to expect that the dilution of a completely dissociated electrolyte, in which the formation of ionic atmospheres is well known to lead to a predominance of attractive over repulsive force, should lead to the evolution of heat. The solution of the paradox depends on the forces exerted by the ions on the dipole molecules of the solvent. N. Bjerrum[41] expresses this by saying that the energy absorbed in increasing separation of the ions with progressive dilution is more than compensated by that evolved as more and more solvent dipole molecules give up their kinetic energy by orientation round the ions, *i.e.*, that the compensating factor is, in effect, the energy released by increased "electrostatic solvation." Such a physical picture cannot, of course, be rigidly deduced from the thermodynamic calculation itself. Examination of the latter shows that the heat of dilution will only have a positive sign when the temperature coefficient of the dielectric constant of the solvent has a sufficiently large negative magnitude to make the term $(1 + T/D \,.\, dD/dT)$ in equation (2) negative. This proviso is equivalent to the condition that the negative value of dD/dT must be large enough to cause the electrical free energy of the solution to increase its numerical (negative) value with rise of temperature (owing to increased electrostatic forces between the ions) sufficiently rapidly to cause the term $T(\partial F_e/\partial T)_v$ to have a larger numerical value than the term F_e in equation (1). Since dD/dT depends, roughly speaking, on the dipole moment of the solvent molecules, it is possible to see in a qualitative way how the thermodynamic condition for positive heats of dilution agrees with Bjerrum's physical picture. An examination of the available dielectric constant data shows that $T/D \,.\, dD/dT$ is algebraically less than -1 in the case of all common ionising solvents, although the values for some solvents of lower dielectric constant, such as acetaldehyde[42] $(D = 21{\cdot}1,\ T/D \,.\, dD/dT = -0{\cdot}88)$ and phosphorus trichloride[43] $(D = 3{\cdot}5,\ T/D \,.\, dD/dT = -0{\cdot}79)$, lead to negative values of the hypothetical heat of dilution of ideal electrolytes dissolved in such media.

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[41] *Z. physikal. Chem.*, 1926, **119**, 145; *A.*, 1926, 476.

[42] P. Drude, *ibid.*, 1897, **23**, 267.

[43] T. M. Lowry, *J.*, 1932, 207; *A.*, 322.

The quantitative test of the theoretical expression in any solvent is of peculiar difficulty for two reasons. First, it involves the measurement of temperature changes of the order of a few millionths of a degree. Secondly, the predicted value of the heat of dilution is extremely sensitive to small errors in the temperature coefficient of the dielectric constant of the solvent, a quantity whose magnitude is very uncertain; even in water the numerical coefficient of equation (3) is subject to an uncertainty, on this account, of about 10%.

Lange and his collaborators have overcome the experimental difficulties with great skill by developing a differential method based on the well-known principle of the twin calorimeter. A Dewar vessel is divided into two halves separated by an insulating diaphragm containing a thermocouple of 1000 junctions, sensitive to temperature differences of 10^{-7°. The dilution is carried out in one half of the vessel while the other half, containing solvent only, serves to balance the effect of the heat of stirring, heat loss due to evaporation, etc. The technique has been refined to the point where heats of dilution can be measured down to 10^{-5} M-concentration. Precision of this order has enabled them to test the theoretical equation within the " limiting range " of Debye–Hückel calculations.

Their measurements cover electrolytes of uni-uni-, bi-uni-, and bi-bi-valency types but have been confined to aqueous solutions. The principal results may be summarised as follows:

(1) The integral heat of dilution is invariably positive at low concentrations.

(2) The integral heat of dilution is proportional to the square root of the concentration up to $M/100$ for uni-univalent electrolytes and over a correspondingly smaller concentration range for the higher valency types. For a minority of salts, such as potassium nitrate, the range of obedience to the square-root relation is a good deal more limited.

(3) Within the limits imposed by our uncertainty as to the value of dD/dT, the limiting slope of V_c plotted against $\sqrt{c}$ agrees with the predicted value.

(4) Even at the lowest concentrations experimentally attainable, small but quite definite differences in limiting slope persist among various salts of the same valency type; this is true of uni-univalent salts and is more marked with ions of higher valency.

The individuality of electrolytes, *i.e.*, their deviation from the ideal behaviour postulated by the Debye–Hückel theory, seems to persist in their thermochemical properties down to concentrations substantially lower than those at which activity and conductivity data suggest virtually ideal behaviour. It is similarly found that at intermediate concentrations thermochemical differences between electrolytes of the same valency type are much more striking than those observed in the activities and conductivities of the same electrolytes.

W. Nernst[44] has sought to account for these deviations by incomplete dissociation of the electrolytes concerned; his view is briefly discussed in the section on " the true degree of dissociation of electrolytes " (p. 27). Lange and his associates prefer to look for their cause in the simplifying assumptions and second-order terms of the purely electrical treatment. In particular, they have explored the possibilities of three refinements in the simplified treatment. Of these, the first is the introduction of a series of a values characteristic of the least distance of approach of the ions, which are no longer assumed to be point charges. The individual values that can be given to this added parameter make it possible to account for differences between electrolytes of the same valency type. Unfortunately, it is found, not only that the sequence in order of magnitude of the necessary a values bears no consistent relationship to the radii of either the ions in the crystal or the solvated ions, but also that the sequence is in some cases the reverse of that which must be adopted to account for the activity data. The second refinement is the introduction of a term for the temperature coefficient of these a values, individual for each electrolyte. This involves a considerable complication in the theoretical treatment; investigation shows that it involves an added negative term which is proportional to the first power of the concentration and therefore unlikely to be of significance at the lowest concentrations at which the individualities persist. The third and final avenue explored by Lange is the possible effect of the electrolyte on the dielectric constant of the solvent. Here again the effect is probably proportional to some higher power than the square root of the concentration so that its significance will be small at high dilutions. Furthermore, E. Lange and A. L. Robinson[45] have shown that, although the addition of urea reduces the temperature coefficient of the dielectric constant of water so much as to lead to the prediction of negative heats of dilution, when aqueous urea solutions are used as a solvent the experimentally determined heat of dilution of potassium chloride in such a solvent is only very slightly different from that of the same salt when dissolved in pure water.

The general conclusion to be drawn from the work of Lange and his collaborators seems to be that, although the positive sign, the variation with concentration, and the valency effect in the heat of dilution of aqueous solutions are in harmony with the interionic attraction theory, certain residual individualities persist in the thermochemical properties of electrolytes at high dilutions for which the electrostatic theory in its present form is unable to account. Thermochemical measurements are seen to constitute a peculiarly sensitive means of exploring deviations from ideal behaviour in electrolytes although it is not, at the moment, at all clear why this should be so. The reason is perhaps to be sought in the peculiarly dominant rôle which ion–solvent forces (as distinct from ion–ion forces) play in heats of dilution.

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[44] W. Nernst, *Z. Elektrochem.*, 1927, **33**, 428; *A.*, 1928, 127.

[45] *J. Amer. Chem. Soc.*, 1930, **52**, 4218; *A.*, 1931, 42.

J. H. W.

4. QUANTUM MECHANICS AND ELECTROCHEMISTRY.

The application of the new ideas of quantum mechanics to electrochemistry has not been long delayed and some preliminary papers recently published suggest that they are likely to give us a much clearer insight into some electrochemical phenomena. The elucidation of electrode processes, of which the thermodynamic account is already eminently satisfactory but whose mechanism has heretofore been obscure, is likely to prove particularly valuable.

A recent paper by R. W. Gurney[46] provides an interesting mechanism for overvoltage as well as sketching a physical picture of the discharge of an ion at an electrode; an important feature of Gurney's mechanism for overvoltage is that the phenomenon is regarded as a *primary* effect and not in any way due to secondary effects such as bubble formation, gas films, or the combination of discharged atoms to form molecules.

Fig. 1 represents the potential-energy curve of an electron along a line joining the surface of an electrode of an inert metal to a neighbouring hydrated cation such as the hydrogen ion. The horizontal lines MM represent the occupied electron levels in the metal, ϕ being the work function of the metal. On the right is the Coulomb field and vacant electron level of the hydrated ion; owing to the positive heat of hydration of the ion W, the distance (E) of this vacant level below the standard level of zero energy is not I, the ionisation potential of the ion-producing atom, but $I - W$; E is the energy evolved when the ion is neutralised.

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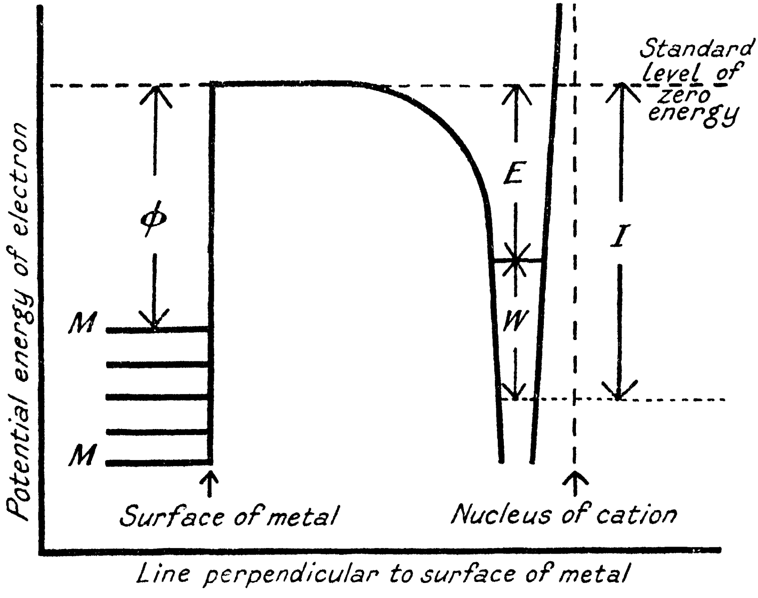
[46] *Proc. Roy. Soc.*, 1931, [*A*], **134**, 137; *A.*, 25. In a second paper (*ibid.*, 1932, [*A*], **136**, 378; *A.*, 699) Gurney deals with the relation between the contact potential difference at a metal–metal interface and the *E.M.F.* of the voltaic cell. His treatment of this subject is interesting but not, however, essentially novel (see, *e.g.*, J. A. V. Butler, *Phil. Mag.*, 1924, **48**, 927; *A.*, 1925, ii, 42).

Although classical mechanics forbids the transition of an electron over the energy barrier, quantum mechanics represents an electron in the metal by a wave-function which does not end abruptly at the surface of the metal but dies away exponentially into the potential barrier. Corresponding to this there is a finite probability of an electron " leaking through " the barrier from the metal into a vacant level of *equal energy* in the neighbouring ion. In the circumstances represented in the diagram (corresponding, *e.g.*, to a platinum electrode dipping in a solution of an acid) neutralisation of the hydrogen ion cannot take place because the vacant level in the ion is higher than the highest occupied electron level in the metal. In order that neutralisation may take place and current may pass through the electrode, the electron levels in the metal must be raised by building up a *negative* (*i.e.*, a " cathodic ") potential in the metal. The negative potential necessary to cause current to flow is determined by the condition $E > \phi - \varepsilon V$.

FIG. 1.



The above picture of the process of discharge of the hydrogen ion is over-simplified in so far as (*a*) the hydration energy is not definite but is spread over a series of energy levels corresponding to a series of vibration levels in the hydrated ion, and (*b*) the metallic electron levels are not all empty above ϕ nor all occupied below. Both of these distributions may be calculated; the former obeys a

Boltzmann distribution, the latter is governed by the Fermi–Dirac statistics.

The condition for the passage of a finite current through the cathode with the liberation of hydrogen (or the discharge of any other cation) is that an appreciable number of high-energy electrons in the metal shall overlap the vacant levels in the positive ion. The variation of this overlap (and the consequent variation in current density) with the cathodic voltage and the temperature is the main object of Gurney's calculations. Having worked out the two distributions indicated above, he has calculated the probability of the transition or leakage of an electron across the potential barrier from the metal to the ion. By integration of this probability between appropriate limits, the current density at the cathode is calculated in terms of the cathodic voltage and the temperature. His result, embodying certain reasonable approximations, is

$$\log i = \frac{E_0 - E_1 + \varepsilon V}{\gamma k T} + \log T + \text{constant}$$

where i is the current density, V the cathodic potential, T the absolute temperature, k the Boltzmann gas constant, $E_0 - E_1 + \varepsilon V$ corresponds to the range of energies over which the probability is integrated, and γ is a small factor greater than unity and, to a first approximation, constant. Differentiating with respect to voltage and temperature respectively, we have $d \log i/dV = \varepsilon/\gamma kT$ and $d \log i/dT = (E_1 - E_0 - \varepsilon V)/\gamma kT^2 + 1/T$. These two equations are in qualitative agreement with F. P. Bowden's experimental observations :[47]

(*a*) that $d \log i/dV = A/T$, where A is independent of the nature of the inert-metal electrode and of whether it is used as anode for the discharge of oxygen or cathode for the discharge of hydrogen and

(*b*) that $d \log i/dT = B$, where B decreases with increasing V. Furthermore, if γ is given the not improbable value of 2, the agreement between $\varepsilon/\gamma k$ and the empirically determined A is excellent. If, in addition, $E_0 - E_1 + \varepsilon V$ (which corresponds to the overlap of energy levels over which the probability is integrated) is set at the reasonable value of one electron-volt, the temperature coefficient of $\log i$ predicted is in good agreement with the observed values of B.

In this way Gurney has shown that two important characteristics of overvoltage, *viz.*, the variation of current density with applied voltage and with temperature, can be adequately and quantitatively accounted for by regarding the determining factor as the probability of the quantum-mechanical transition of an electron from the electrode to the cation to be discharged (or from the anion to be discharged to the electrode).

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[47] *Proc. Roy. Soc.*, 1929, [*A*], **125**, 446; *A.*, 1929, 1391; *ibid.*, **126**, 107; *A.*, 1930, 169.

Another application of quantum mechanics to an electrochemical problem is to be found in a paper by L. Farkas [48] on the conductivity of concentrated solutions of sodium in liquid ammonia. It is well known that, as the concentration of such a solution increases, the equivalent conductivity at first diminishes proportionally to the square root of the concentration, corresponding to electrolytic conduction by sodium ions and probably solvated electrons; at a concentration about $0{\cdot}1M$, the equivalent conductivity passes through a minimum and then increases very rapidly until in saturated solution the specific conductivity is comparable with that of liquid mercury. Corresponding to this rise in conductivity, the contribution of the sodium ions to the carriage of the current diminishes rapidly and becomes insignificant in the more concentrated solutions.

Heretofore the rise in equivalent conductivity in concentrated solution has received only a qualitative explanation which attributes it to the increasing proportion of free unsolvated electrons as the concentration of sodium in the solution rises. The shift in the equilibrium between free and solvated electrons with increasing concentration necessary to account for the observed rise in equivalent conductivity is so great as to render this explanation far from probable.

Farkas attributes the conductivity in concentrated solution to the quantum-mechanical transition of electrons between neighbouring sodium atoms, which under the influence of an applied potential gradient will take place more frequently towards the anode than towards the cathode. Fig. 2 represents the potential-energy curve of an electron relative to two sodium atoms in a uniform potential gradient such that the anode lies to the left of the figure. I is the ionisation potential of the sodium atom, d_c is the distance between the two sodium atoms, and the applied potential gradient is equal to $(\tan\theta)/(\text{electronic charge})$. The probability of an electron transition in either direction by leakage through the potential barrier can be calculated by the Gamow–Condon–Gurney formula and expressed in terms of the above quantities together with the mass of the electron (m), the principal quantum number (n), and the orbital radius (r) of the outermost electron in the sodium atom, the concentration of the solution (c), the Avogadro number (N), and Planck's constant (h). By subtracting the two probabilities, the excess of electron transitions towards the anode can be calculated, and hence the specific conductivity. To a first approximation the result is

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[48] *Z. physikal. Chem.*, 1932, [*A*], **161**, 355.

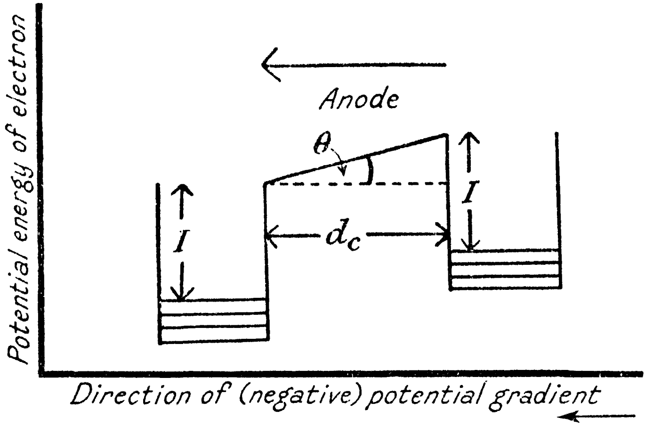
$$\kappa = \frac{n\pi}{\sqrt{2m} \, . \, r^2} \cdot \frac{\varepsilon^2 d_c^3}{\sqrt{I}} \cdot \frac{cN}{1000} e^{-4\pi\sqrt{2m}\sqrt{I}d_c/h}$$

If it is now assumed that the sodium atoms are distributed regularly through the solution as in a simple cubic lattice,* the distance apart of the atoms d_c at a concentration c is given by

$$d_c = 1/\sqrt[3]{c \times 6 \times 10^{20}}$$

Putting n equal to 3, r equal to $1{\cdot}7 \times 10^{-8}$, and giving the universal

FIG. 2.


Potential energy of electron
Anode
θ
I
I
d_c
Direction of (negative) potential gradient

constants their numerical values, we obtain the following expression for the specific conductivity at concentration c

$$\kappa_c = 3{\cdot}10 \times 10^{11} \cdot \frac{1}{\sqrt{I}} 10^{-4{\cdot}2 \times 10^6\sqrt{I}/\sqrt[3]{c}}$$

This equation leads to a curve of specific conductivity against concentration very similar to but slightly steeper than that observed experimentally. The value of I necessary to give the observed numerical values lies between 9000 and 10,000 calories per mol.; this is about 12 times as small as the ionisation energy *in vacuo*, whereas the dielectric constant of liquid ammonia is about 22. In view of the approximate nature of the calculations and the absence of arbitrary constants, the concordance is as good as could be expected.

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* This assumption is essential to the theory. If the atoms are distributed *over a range of distances* apart, the small number of atoms near the minimal distance will play a dominant part in the quantum-mechanical transitions and the probability of occurrence of this distance will change too slowly with increasing concentration to account for the experimental facts.

In spite of the somewhat arbitrary assumption of lattice-like distribution of atoms in the solution, as well as the fundamental difficulty (which is also met with in the theory of the conductivity of metals) that each atom in the lattice is regarded at one and the same time as ionised (in order that it may receive an electron) and un-ionised (in order that it may give up an electron), the quantitative success of the calculation is sufficient to make it of great interest as an application of quantum mechanical principles to conductivity. J. H. W.

5. Chemical Kinetics.

The study of chemical kinetics depends essentially upon observation of the progress of chemical reactions with time. Thence, conclusions can often be drawn, on the one hand, about the nature of transiently formed intermediate products, and on the other, about the physical laws determining molecular transformations. In both these respects the application of spectroscopic methods has yielded information in a much more direct manner than kinetic measurements could, and, in the second matter, quantum-mechanical theories can be of great assistance in predicting which kinds of atomic and molecular processes are possible or probable. As an example of the elucidation of reaction mechanisms by spectroscopic means, it is enough to refer to the identification of the various atoms, radicals, or molecules concerned in the emission of flame spectra (see p. 59). To illustrate the application of such means in the discovery of the physical nature of molecular transformations, we need only take the investigation of photochemical primary processes (cf. following section).

A theoretical classification of chemical rearrangements or decompositions, which seems likely to prove of great importance, is that which distinguishes " adiabatic " from non-adiabatic processes. The former kind occur with an accompanying electron transition, the latter without, and there are important differences between them. The following is an example. According to G. Herzberg,[49] the molecule of nitrous oxide has a singlet ground state, while N_2 and O would correspond to a triplet state. Hence, if N_2O changes into $N_2 + O$, there must be an electron transition, in fact the unimolecular decomposition of the nitrous oxide molecule would have to be a " predissociation." It is believed that " radiationless changes " of this kind ordinarily occur between states of the same multiplicity. " Intercombinations " can occur, but with a much smaller probability. Thus the life of an activated nitrous oxide molecule should be abnormally long, before chemical transformation takes place. Nitrous oxide absorbs continuously from 2000 Å. to 1680 Å. and from 1550 Å. to the edge of the Schumann region. It is transparent at longer wave-lengths, although the energy of removal of an oxygen atom is not great. These facts illustrate the non-dissociability of nitrous oxide into N_2 and O in a primary photochemical act. Presumably, we must reckon with the occurrence of non-adiabatic transformations also in the reactions of more complex molecules: some of these changes may be "forbidden" or associated with very small probabilities. The modification of the transformation probabilities by the "perturbing" action of external forces may be one important factor in "catalytic" phenomena. But in any example of even moderate complexity *a priori* calculations are almost hopelessly difficult, so that it is probable that only direct kinetic experiments can decide how important factors of this kind really are. The general theoretical treatment of adiabatic and non-adiabatic chemical processes is, however, exemplified in the papers of F. London,[50] and of H. Pelzer and E. Wigner.[51] The latter authors, discussing reactions of the type $A + BC = AB + C$, show that the probability of electronic excitation during the chemical reaction is small when the lowest "energy surface" is far removed from the others. (Diagrams can be plotted giving the potential energy of the system for all relative positions of the atoms, as in the work of Eyring and Polanyi referred to in last year's Report. These are the energy surfaces: there will be a different one for each of the possible states of electronic excitation of the system.)

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[49] *Z. physikal. Chem.*, 1932, [*B*], **17**, 68; *A.*, 680; cf. also R. Mecke, *ibid.*, **18**, 53; *A.*, 915.

In previous reports [52] the question of quantum-mechanical passage through energy barriers has been mentioned. It appears that usually, or at any rate in examples of chemical interest, transition probabilities calculated by means of this kind of theory do not differ very much from the classical probability of passage over the energy barrier. The transition probability contains a factor involving the negative exponential of the mass of the particle penetrating the barrier, the mass coming in from the mass term in the original Schroedinger equation.[53] When the particle is an electron, the non-classical transition probabilities become very high. When the particle has the mass of an ordinary atom, the classical and the non-classical probability become much closer. R. P. Bell [54] has pointed out, however, that the hydrogen atom, or proton, occupies an exceptional position, and that, owing to its small mass, appreciable deviations from classical behaviour may be expected. Among the consequences of these deviations is a departure from the Arrhenius equation for the variation of reaction velocity with temperature, in the sense that at lower temperature, higher values would be found for the reaction rate than those predicted by the equation. As Bell points out, no really suitable data for testing this exist. Spurious deviations from the Arrhenius equation [55] are of course quite common, so that it may be all too easy to " confirm " the operation of quantum-mechanical factors in this particular field.

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[50] *Z. Physik*, 1932, **74**, 143; *A.*, 324.

[51] *Z. physikal. Chem.*, 1932, [*B*], **15**, 445; *A.*, 343.

[52] *Ann. Reports*, 1930, **27**, 26; 1931, **28**, 23.

[53] Cf. Gamow, "Atomic Nuclei," Oxford, 1931.

[54] *Proc. Roy. Soc.* (in the press).

From what has been said above about the application of methods and theoretical ideas more or less connected with spectroscopy to the problems of kinetics, it might be inferred that the more ordinary methods of investigation were largely superseded, but this would hardly be a well-balanced judgment. The difficulty or even ambiguity of quantum-mechanical calculations in examples which are not almost ideally simple will probably restrict their function to stimulating or interpreting rather than replacing or anticipating direct experiment. Moreover, methods which depend upon theoretical calculations or upon spectroscopic identification of intermediate products can only assist in understanding details of mechanism, and this knowledge is not of much use unless interest in the descriptive chemistry of the complete process is presupposed. The actual unfolding of phenomena in time has always been considered worth observing for its own sake, whether by the contemplation of complex emergent qualities which make the changing picture of nature as a whole, or by the scientific study of recondite constituents of this picture, such as chemical reactions.

An interesting piece of descriptive chemistry has been growing up in connexion with reactions in the solid state, the type of change most convenient for investigation being that where one solid yields another solid and a gas.[56] It is not usual that the second solid forms solid solutions in the first. This means that molecules or ions of the second are more stable when placed in their own space lattice than when uniformly disseminated among the molecules or ions of the initial substance. Consequently, the chemical change can take place more easily if there is ready formed some of the lattice of the reaction product to which fresh elements can attach themselves. Thus reactions of this kind usually spread from nuclei. These nuclei seem first to be formed on the surface of the crystals. The conditions governing their formation are independent of those determining the rate at which they grow as the newly formed crystal face advances through the unchanged material. The nuclei can be "poisoned" and prevented from growing by the action of foreign gases in the system.[57] As the chemical change progresses, the extent of the interface between original substance and reaction product alters and the rate of reaction thus varies in a complex manner. The shape of the curve representing the extent of reaction as a function of time depends upon the rate at which fresh nuclei are formed relative to the rate of growth of existing nuclei. When the change spreads from a limited number of nuclei for each particle of the solid, the rate increases with time in an "autocatalytic" manner, and passes through a maximum. It is possible by careful analysis of the form of the curves to draw conclusions, on the one hand, about the rate of advance of the crystal face and, on the other, about the kind of nucleation process occurring.[58]

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[55] *E.g.*, those due to the existence of two concurrent reactions with different energies of activation.

[56] Among systems recently investigated are $CuSO_4,5H_2O \longrightarrow CuSO_4,H_2O + 4H_2O$, M. L. Smith and B. Topley, *Proc. Roy. Soc.*, 1931, [*A*], **134**, 224, *A.*, 26; $Ag_2CO_3 \rightleftharpoons Ag_2O + CO_2$, W. D. Spencer and B. Topley, *J.*, 1929, 2633; *Trans. Faraday Soc.*, 1931, **27**, 94.

When the rate of advance of the new crystal face is known as a function of temperature, it is possible to attempt a correlation of the absolute rate of reaction and the "energy of activation," and so to test hypotheses about the mechanism by which the new phase grows. The complete answer to the question of mechanism has not yet been found, but Topley [59] has recently made an interesting exploration of possibilities, and concludes that, for the dehydration of copper sulphate pentahydrate to monohydrate, "it appears that it is just possible to account for the observed rate, if four degrees of freedom in the complex cation are taken into account, and regarded as strongly coupled through the central $Cu^{\bullet\bullet}$ ion; in addition, a very rapid redistribution of energy inside the activated complex is required."

In a review [60] of chemical kinetics in 1927, reference was made to the fact that a number of bimolecular reactions in solution proceed at rates very much smaller than those given by the expression, (number of collisions) × $e^{-E/RT}$, which predicts the correct order of magnitude for a considerable number of gas reactions depending on collisions between fairly simple molecules. At that time the discrepancy was thought to be due to a deactivating influence of solvent molecules. There proves, however, to be no such general deactivating influence. In the first place, the decomposition of chlorine monoxide [61] and the interaction of ozone and chlorine [62] have been shown to occur at nearly the same rate in solution in carbon tetrachloride as in the gas phase : thus reactions depending on the co-operation of two molecules are not necessarily interfered with by the solvent. Secondly, it has been found that two reactions, namely, the combination of triethylamine and ethyl iodide, and the esterification of acetic anhydride by ethyl alcohol, both of which are "abnormally slow" to the extent of many powers of ten in hexane or in carbon tetrachloride solution, do not take place any more rapidly in the gas phase.[63] (Indeed, even such reaction as the vapours undergo may be confined to the glass surface of the vessel.) Thus again it appears that, whatever the anomaly may be, it is not directly connected with solvent action. It also appears that the "abnormally slow" reactions in solution are not necessarily the most characteristic. Further investigation of the literature [64] reveals the existence of a considerable number taking place at about the rate predicted by the simple formula, and of a further class in which the rate is many times greater. To account for these latter it is necessary to assume the participation of varying numbers of internal degrees of freedom in the activation mechanism, as with gaseous reactions of rather complex molecules. What causes underlie the wide variations on either side of what might be called "standard behaviour" of bimolecular reactions in solution is an interesting problem, about which various views are possible. But the time is hardly ripe for discussing them.

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[57] *E.g.*, the silver nuclei in the system $Ag_2C_2O_4 \longrightarrow 2Ag + 2CO_2$ are "poisoned" by oxygen.

[58] B. Topley and J. Hume, *Proc. Roy. Soc.*, 1928, [*A*], **120**, 211 (for the decomposition of calcium carbonate hexahydrate in contact with water); R. S. Bradley, J. Colvin, and J. Hume, *ibid.*, 1932, [*A*], **137**, 531; *A.*, 1094 (for the same system and for the dehydration of potassium hydrogen oxalate hemihydrate).

[59] *Proc. Roy. Soc.*, 1932, [*A*], **136**, 413; *A.*, 702 (for further references, see this paper).

[60] *Ann. Reports*, 1927, **24**, 314.

Many of the subjects discussed in these reports in the last few years are still rapidly developing, and it is impossible to do justice to more than a quite arbitrarily selected few. H. von Hartel, N. Meer, and M. Polanyi have made an exhaustive study of the interaction of alkyl chlorides and sodium vapour with the object of finding out how the ease of reaction varies with the structure of the chloride.[65] As is well known, Polanyi found that in many reactions between alkali metals and halogen compounds, nearly every collision led to reaction, *i.e.*, that the heat of activation is zero, or, in other words, that there is no "inertia." Later, he discovered that there is an increase in inertia as the series methyl iodide, bromide, chloride, fluoride is traversed. The following general rules now seem to emerge: there is a decrease in inertia with increasing length of the hydrocarbon chain, with passage from primary through secondary to tertiary compounds, with increase in the number of chlorine atoms present, and with introduction of a carbonyl group. A double bond on the carbon atom bearing the chlorine hinders reaction, while one on the next carbon atom decreases the inertia. In another paper, N. Meer and M. Polanyi [66] make a comparison of these structural influences in the gaseous reactions with those found for a variety of organic reactions in solution: in a general way a parallelism appears, which is very suggestive.

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[61] E. A. Moelwyn-Hughes and C. N. Hinshelwood, *Proc. Roy. Soc.*, 1931, [*A*], **131,** 177.

[62] E. J. Bowen, E. A. Moelwyn-Hughes, and C. N. Hinshelwood, *ibid.*, **134,** 211; *A.*, 25.

[63] E. A. Moelwyn-Hughes and C. N. Hinshelwood, *J.*, 1932, 230.

[64] E. A. Moelwyn-Hughes, *Phil. Mag.*, 1932, [vii], **14,** 112; *A.*, 916; *J.*, 1932, 95; *A.*, 233; *Chem. Reviews*, 1932, **10,** 241.

The number of known unimolecular gaseous reactions increases steadily, as was only to be expected as soon as the idea of exploring the unlimited field of organic substances arose. Perhaps the most interesting of these recently investigated is the decomposition of ethyl bromide.[67]

The first of the organic unimolecular gas reactions to be found was the decomposition of acetone. There has always been some discussion about the chemical steps in this reaction. The first suggestion was that carbon monoxide separates from the molecule, leaving two methyl residues, the interaction of which determines the other products. Subsequently, it has been maintained that the decomposition must take place by way of keten formation. It now appears [68] that when acetone vapour is passed through a tube at 800—1000°, methyl radicals can be detected by the Paneth metal mirror method. It even seems that the temperature coefficient of the rate of decomposition into methyl radicals is about the same as that of the rate of the ordinary thermal decomposition. Thus the idea of a primary splitting into CO and $2CH_3$ seems, after all, to have something to be said for it.

Some years ago Wulf and Tolman concluded, on energetic grounds, that the decomposition of ozone could not take place by the Jahn mechanism $O_3 \rightleftharpoons O_2 + O$, $O_3 + O = 2O_2$. Much more reliable values for the heat of dissociation of oxygen are now available, and, in point of fact, are much smaller than was formerly supposed. Recalculation [69] using the newer values rehabilitates the Jahn mechanism as at least an energetically possible one. It may be said, in general, that the decrease in the accepted values for the heats of dissociation of the simpler diatomic molecules places a number of kinetic problems in quite a new light, and some reorganisation of our views on molecular decompositions in thermal reactions may soon be occurring.

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[65] *Z. physikal. Chem.*, 1932, [*B*], **19**, 139.

[66] *Ibid.*, p. 164.

[67] E. L. Vernon and F. Daniels, *J. Amer. Chem. Soc.*, 1932, **54**, 2563; *A.*, 815.

[68] F. O. Rice, W. R. Johnston, and B. L. Evering, *ibid.*, p. 3529; *A.*, 1108.

From the nature of the method employed in its investigation, the dissociation of nitrogen tetroxide into the dioxide during the passage of sound waves is specially interesting. According to W. T. Richards and J. A. Reid,[70] the velocity constant at 25° and 260 mm. is about $4{\cdot}8 \times 10^4$, while P. D. Brass and R. C. Tolman [71] give 2—8×10^4 sec.$^{-1}$ at 25° and 1 atmosphere. The activation energy appears to approximate to the heat of dissociation of the tetroxide, as would be expected.

Finally, before we turn to the consideration of photochemical reactions, brief reference may be made to recent work on chain reactions, and in particular to the study of the remarkable phenomenon of explosive combination between two critical pressure limits. The work of different investigators can be correlated much more easily if, in applying the branching-chain hypothesis, we recognise that the conditions necessary for the actual starting of chains may be quite independent of those which govern their propagation through a gas mixture.[72] There is in a rough way an analogy between this and the phenomenon of change of state, where the presence of nuclei may be necessary, but where the rate of growth of the nuclei depends only upon the temperature and pressure or composition of the surrounding material. Sometimes the first centres from which a branching-chain explosion develops are formed on the wall of the vessel by a heterogeneous reaction.[73] If the catalytically active parts of the wall are poisoned the chains cannot start. The system is then in a "metastable" state.[74] Given, however, that some chains do start, the condition for their branching may be determined entirely by the temperature and composition of the gas mixture, as it appears to be in the neighbourhood of "upper limits."

The initiation of chains by surface reactions has been studied by H. W. Melville and E. B. Ludlam [75] for the case of phosphorus vapour and oxygen and by A. Ritchie and Ludlam for sulphur and oxygen.[76] The initiation of explosion in hydrogen–oxygen mixtures by the introduction of artificially produced hydrogen atoms has been studied by F. Haber and F. Oppenheimer.[77] The influence of inert gases on the diffusion of chain-carrying species to the wall has been further investigated by H. W. Melville,[78] by A. Ritchie, R. R. H. Brown, and J. J. Muir,[79] and by H. W. Thompson,[80] and others, the results being on the whole in agreement with what might be expected theoretically. The slow oxidation of moist carbon monoxide has been studied by G. Hadman, H. W. Thompson, and C. N. Hinshelwood,[81] who find evidence that chains of great length, initiated by hydrogen from the water-gas reaction, are propagated.

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[69] O. R. Wulf, *J. Amer. Chem. Soc.*, 1932, **54**, 156; *A.*, 344.

[70] *Ibid.*, p. 3014; *A.*, 916. [71] *Ibid.*, p. 1003; *A.*, 474.

[72] G. Hadman, H. W. Thompson, and C. N. Hinshelwood, *Proc. Roy. Soc.*, 1932, [*A*], **138**, 297.

[73] H. N. Alyea and F. Haber, see *Ann. Reports*, 1930, **27**, 45.

[74] See (72). [75] *Proc. Roy. Soc.*, 1932, [*A*], **135**, 315; *A.*, 477.

From a more general point of view, it should be mentioned that alternatives to the chain theory of reactions showing explosion limits are not being ignored. The problem of how far it would be possible to construct a purely thermal theory of the whole group of phenomena is being explored. Preliminary discussions of this matter have been published.[82] On the whole, it appears to the reviewer that at the present moment the chain theory is the most convenient and satisfactory, though the alternatives are not conclusively disposed of and may still prove to have important elements of truth in them. C. N. H.

6. PHOTOCHEMISTRY.

Technique.—The advent of the spectroscopist in the field of photochemistry has emphasised the need for more precise technique in the examination of photoreactions, particularly in connexion with the use of monochromatic illumination and very exact quantum-efficiency measurements. Thus, much attention has been given to the construction of suitable light sources, monochromators, and to methods of measurement. F. B. Bowden and C. P. Snow [83] have used a simple type of large monochromator, constructed, however, of quartz crystal parts of a size extremely difficult to obtain. F. Daniels and L. J. Heidt [84] describe a much more elaborate type of monochromator with optical parts of fused quartz, to be used in conjunction with a new type of mercury lamp of very high intrinsic intensity.[85] With such lamps and the monochromator the emission lines in the ultra-violet can be isolated with an intensity ample for photochemical work, though the shorter wave-lengths suffer through absorption by the fused quartz. Similar intensities without such good monochromatism of the ultra-violet mercury lines can be obtained from an ordinary mercury lamp with condenser-filters.[86] Accurate calibration of such ultra-violet light is best performed by actinometry,[87] for the surface thermopile has been shown to be subject to large errors in ordinary use.[88] H. Klumb and T. Haase [89] have shown that glass windows 10μ thick are as transparent as quartz to the ultra-violet, and can be made strong enough to be useful in photochemical work. The most suitable light source for the region about 2000 Å. is the condensed spark discharge. G. S. Forbes and F. P. Brackett [90] describe a device for ensuring the constancy of this source, for which monochromatism can be obtained by means of "focal isolation." [91] Very intense light of shorter wave-lengths (1469—1295 Å.) can now be obtained from a new rare-gas lamp.[92]

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[76] *Proc. Roy. Soc.*, 1932, [*A*], **138**, 635.

[77] *Z. physikal. Chem.*, 1932, [*B*], **16**, 443; *A.*, 576.

[78] *Trans. Faraday Soc.*, 1932, **28**, 308, 814; *A.*, 701.

[79] *Proc. Roy. Soc.*, 1932, [*A*], **137**, 511; *A.*, 1093.

[80] *Trans. Faraday Soc.*, 1932, **28**, 299; *A.*, 701.

[81] *Proc. Roy. Soc.*, 1932, [*A*], **137**, 87.

[82] C. N. Hinshelwood, *Trans. Faraday Soc.*, 1932, **28**, 184; see also (72).

[83] *Nature*, 1932, **129**, 720; *A.*, 656.

[84] *J. Amer. Chem. Soc.*, 1932, **54**, 2381, 2384.

Predissociation and Photodissociation (see *Ann. Reports*, 1930, **27**, 21).—The most important photochemical problem of the moment is the elucidation of the mechanism of the photoreactions of simple molecules in the gaseous state by the correlation of photochemical data with spectral observations. It has generally been assumed that a considerable change in the quantum efficiency of a photoreaction, and possibly in the nature of the products formed, would occur as the wave-length of the exciting light passes from one side to the other of spectral thresholds (predissociational or photodissociational).[93] In the case of nitrogen dioxide the spectral predissociation threshold at 3800 Å. is associated with a very striking photochemical threshold,[94] but more recently examined reactions have not shown such simple behaviour. The absorption spectrum of chlorine dioxide exhibits a predissociation threshold at 3753 Å., and though precise measurements of the rate of photodecomposition in the gaseous state are difficult to make owing to the variable effects of secondary reactions, there does not appear to be a change in the quantum efficiency as the threshold is crossed.[95] Experiments on chlorine dioxide in solution indicate that a photochemical threshold does exist on the long-wave side of the spectral one at a distance from it farther than would be expected from the mere influence of the solvent.[96] Contrary to earlier expectations,[93] no marked photochemical thresholds associated with the spectral predissociation limits have been found for the photodecomposition of aldehydes. Working with gaseous formaldehyde, which shows a predissociation limit at about 2750 Å., R. G. W. Norrish and F. W. Kirkbride [97] found no change either in the quantum efficiency of photodecomposition or in the nature of the products in spectral regions on each side of the threshold. The products were found to be $H_2 + CO$, and the quantum efficiency unity—facts which do not agree with the older view that the photoreaction is essentially $H_2CO + h\nu \longrightarrow H_2CO^{\times} \longrightarrow H + HCO$. The results of P. A. Leighton and F. E. Blacet [98] are similar. They studied the photodecomposition of propionaldehyde in monochromatic light from 3130 to 2537 Å. This wave-length range brackets a spectral threshold at about 3250 Å. between a predissociational absorption spectrum and a continuous one.* They confirmed earlier work on aldehydes, that two photoprocesses occur, (*a*) decomposition, and (*b*) polymerisation; that the decomposition process is chiefly of the type $RHCO \longrightarrow RH + CO$, accompanied by the formation of only a small amount of hydrogen and the hydrocarbon R_2; and that, while the decomposition is unimolecular, the polymerisation is bimolecular. The quantum efficiencies of dissociation and of polymerisation were separately estimated; the former, independent of pressure, varied from 0·5 to 1·0 between 3130 and 2537 Å., while the latter, depending directly on the pressure, reached values of 0·7 at 200 mm. pressure in the same spectral range. At high pressures, therefore, the total quantum efficiency attains values well above unity, and further, fluorescence of the vapour was observed, indicating the production of non-dissociating excited molecules.[99] These facts go to show that the original application of the theory of predissociation to photochemistry was too simplified. In an important paper on the predissociation of polyatomic molecules, J. Franck, H. Sponer, and E. Teller [1] provide an explanation of many of the difficulties. In the original theories of predissociation the following considerations were not taken into account:

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[85] See also P. A. Leighton and F. E. Blacet, *J. Amer. Chem. Soc.*, 1932, **54**, 3165; and R. H. Crist, *ibid.*, p. 3939. For capillary lamps containing Bi, Cd, Pb, Tl, and Zn, see R. H. Hoffman and F. Daniels, *ibid.*, p. 4226.

[86] E. J. Bowen, *J.*, 1932, 2236; *A.*, 1013.

[87] G. S. Forbes, G. B. Kistiakowsky, and L. J. Heidt, *J. Amer. Chem. Soc.*, 1932, **54**, 3246; *A.*, 1013; W. G. Leighton and G. S. Forbes, *ibid.*, 1930, **52**, 3139; *A.*, 1930, 1260.

[88] P. A. Leighton and W. G. Leighton, *J. Physical Chem.*, 1932, **36**, 1882; *A.*, 924.

[89] *Z. Physik*, 1932, **76**, 322.

[90] *J. Amer. Chem. Soc.*, 1931, **53**, 3973.

[91] E. O. Wiig and G. B. Kistiakowsky, *ibid.*, 1932, **54**, 1806; *A.*, 705.

[92] P. Harteck and F. Oppenheimer, *Z. physikal. Chem.*, 1932, [*B*], **16**, 77.

[93] G. Herzberg, *Trans. Faraday Soc.*, 1931, **27**, 378; R. Mecke, *ibid.*, p. 359; *A.*, 1931, 1136; see also "Discussion on the Critical Increment of Homogeneous Reactions," Chem. Soc., Dec., 1931, pp. 15—21, 50—61.

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* The threshold between the predissociational and fine-structure spectrum is unknown for this aldehyde.

[94] R. G. W. Norrish, *J.*, 1929, 1158, 1604, 1611; *A.*, 1929, 893, 1022.

[95] W. Finkelnburg and H. J. Schumacher, *Z. physikal. Chem.*, Bodenstein Festband, 1931, 740; *A.*, 1931, 1210; J. W. T. Spinks, *J. Amer. Chem. Soc.*, 1932, **54**, 1689; *A.*, 581.

[96] E. J. Bowen and W. M. Cheung, *J.*, 1932, 1200; *A.*, 581.

[97] *J.*, 1932, 1518; *A.*, 706.

[98] *J. Amer. Chem. Soc.*, 1932, **54**, 3165; *A.*, 1006.

(1) Certain apparent spectral predissociation limits are not associated with unimolecular decompositions but are caused by the abnormal broadening of the rotational lines through collisions, *i.e.*, collisions cause the transformation of the excited molecules into another neighbouring state whose potential energy-distance curve does not cut that of the first. The so-called predissociation limit of sulphur dioxide at 2800—2600 Å. is of this type, and this explains why this gas does not undergo photochemical change until the higher predissociation limit at 1950 Å. is approached,[2] and why fluorescence is observed in it at about 2000 Å.

(2) When account is taken of the vibrational and rotational energy of the products of the predissociation of *polyatomic* molecules, an explanation is provided of the fact that in such cases the spectral limit is not sharp; *e.g.*, for NO_2 the lower limit reaches from 4000 to 3000 Å. The exact value of a recorded limit thus varies with the experimental conditions of its observation.

(3) Predissociation can be induced or increased by collisions in some cases; *e.g.*, deviations from Beer's law occur in Br_2 and NO_2 vapour,[3] and iodine atoms are detectable in I_2 vapour at wavelengths less than 5100 Å. if argon is present, the argon simultaneously quenching the fluorescence of the higher vibrational states of the I_2 molecule.[4]

(4) Predissociational and photodissociational processes, and probably, in general, non-dissociating and dissociating processes, of activation can interpenetrate one another, as in the case of iodine chloride.[5]

The sum total of these considerations shows that great care must be used in interpreting spectral limits, so much so that, instead of spectroscopy providing an easy answer to photochemical problems, it now seems that the photochemist may be able through refined work to help the spectroscopist.

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[99] G. Herzberg and K. Franz (*Z. Physik*, 1932, **76**, 720; *A.*, 896) have also observed fluorescence of formaldehyde vapour.

[1] *Z. physikal. Chem.*, 1932, [*B*], **18**, 88; *A.*, 896.

[2] (Frl.) G. Kornfeld and E. Weegmann, *Z. Elektrochem.*, 1930, **36**, 789; *A.*, 1930, 1383; K. Wieland, *Nature*, 1932, **130**, 847.

[3] V. Kondratéev and L. Polak, *Z. Physik*, 1932, **76**, 386; *A.*, 791.

[4] L. A. Turner, *Physical Rev.*, 1932, [ii], **41**, 627.

[5] W. G. Brown and G. E. Gibson, *ibid.*, **40**, 529; *A.*, 791.

A number of reactions of the dissociation type have been studied, and mechanisms proposed for the total change in different cases, including the photodecomposition of chlorine monoxide,[6] of ozone in red and ultra-violet light,[7] the alkyl iodides,[8] hydrazine,[9] phosphine[10] and carbonyl sulphide.[11] The mechanism of decomposition of the ammonia molecule has been thoroughly investigated,[12] the small quantum yield being due to back reaction,[13] and traces of hydrazine being also formed.[14]

Chain Reactions and Photosensitisation.—The photoreaction between hydrogen and chlorine continues to receive attention. The hydrogen-atom concentration during reaction has been estimated by making use of the two forms of hydrogen.[15] Its temperature coefficient has been investigated.[16] An important new observation which explains certain of the baffling features of this reaction has been made by R. W. G. Norrish and M. Ritchie.[17] By the use of a light-absorption technique for following the reaction, they have shown that the hydrogen chloride formed exerts a large inhibiting effect. New results fail to confirm earlier work on the inhibiting effect of drying.[17a] Calculations based on wave-mechanics indicate that when halogens are dissociated by light the free atoms combine with other molecules giving, *e.g.*, Cl_3;[18] at the same time, the heats of activation of the reactions :

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[6] W. Finkelnburg, H. J. Schumacher, and G. Stieger, *Z. physikal. Chem.*, 1931, [*B*], **15**, 127; *A.*, 227.

[7] H. J. Schumacher and U. Beretta, *ibid.*, 1932, [*B*], **17**, 405, 417; *A.*, 820.

[8] G. Emschwiller, *Compt. rend.*, 1931, **193**, 1003; *Ann. Chim.*, 1932, [x], **17**, 413; *A.*, 29, 706; W. West and (Miss) B. Paul, *Trans. Faraday Soc.*, 1932, **28**, 688; *A.*, 1007.

[9] R. R. Wenner and A. O. Beckman, *J. Amer. Chem. Soc.*, 1932, **54**, 2787; *A.*, 918.

[10] H. W. Melville, *Nature*, 1932, **129**, 546; *A.*, 479.

[11] W. Lochte-Holtgreven, C. E. H. Bawn, and E. Eastwood, *ibid.*, p. 869; *A.*, 820.

[12] E. O. Wiig and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, 1932, **54**, 1806; *A.*, 705.

[13] H. W. Melville, *Trans. Faraday Soc.*, 1932, **28**, 885.

[14] G. R. Gedye and E. K. Rideal, *J.*, 1932, 1160; *A.*, 581.

[15] K. H. Geib and P. Harteck, *Z. physikal. Chem.*, 1931, [*B*], **15**, 116; *A.*, 237.

[16] E. Hertel, *ibid.*, p. 325; *A.*, 348.

[17] *Nature*, 1932, **129**, 243; *A.*, 348.

[17a] W. H. Rodebush and W. C. Klingelhofer, *Proc. Nat. Acad. Sci.*, 1932, **18**, 531; A. J. Allmand and H. C. Craggs, *Nature*, 1932, **130**, 927.

$$\begin{aligned} Cl_3 + H_2 &\longrightarrow Cl_2 + HCl + H \\ H + Cl_2 + H_2 &\longrightarrow 2HCl + H \\ Cl + H_2O + H_2 &\longrightarrow HCl + H_2O + H \end{aligned}$$

as estimated by the methods of wave-mechanics are such that none of them is likely to occur in the hydrogen–chlorine photoreaction.[19] The photochlorination of tetrachloroethylene is strongly inhibited by oxygen, and in presence of excess of the latter substance the chief products are trichloroacetyl chloride and carbonyl chloride.[20] Further study of the chlorination of such hydrogen-free molecules in the presence and absence of oxygen is likely to clear up many difficult points in the mechanism of chlorination processes. Chain mechanisms for the photosensitised decompositions by chlorine for nitrogen trichloride[21] and of ozone[22] have been proposed to explain the experimental results.

Miscellaneous Photochemical Reactions.—A surprising observation of importance in theories of autoxidation is that illumination of oxygen-free alkali sulphite solutions results in the liberation of gaseous hydrogen.[23] The photochemical decomposition of organic acids in the vapour state and in solution appears to be not a simple process.[24] In the photo-oxidation of aliphatic alcohols by acid solutions of dichromate the photo-active ion is $HCrO_4'$, and the primary reaction probably gives aldehyde and quadrivalent chromium.[25] In marked contrast to this result, the photo-oxidation of quinine by dichromic acid is governed by the light absorption of the quinine molecule.[26] Two reactions, whose rates have earlier been found to vary as the square root of the light intensity, can by simplification of the conditions be made to obey the equivalence law.

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[18] G. K. Rollefson and H. Eyring, *J. Amer. Chem. Soc.*, 1932, **54**, 170; *A.*, 348.

[19] G. E. Kimball and H. Eyring, *ibid.*, p. 3876.

[20] R. G. Dickinson and J. A. Leermakers, *ibid.*, p. 3852.

[21] J. A. G. Griffiths and R. G. W. Norrish, *Proc. Roy. Soc.*, 1931, [*A*], **130**, 591; 1932, [*A*], **135**, 69; *A.*, 349.

[22] A. J. Allmand and J. W. T. Spinks, *J.*, 1932, 599; *A.*, 348.

[23] F. Haber and O. H. Wansbrough-Jones, *Z. physikal. Chem.*, 1932, [*B*], **18**, 103; *A.*, 1006.

[24] L. Farkas and O. H. Wansbrough-Jones, *ibid.*, p. 124; *A.*, 1006; W. C. Pierce and G. Morey, *J. Amer. Chem. Soc.*, 1932, **54**, 467; *A.*, 480.

[25] E. J. Bowen and J. E. Chatwin, *J.*, 1932, 2081; *A.*, 1006.

[26] G. S. Forbes, L. J. Heidt, and C. G. Boissonnas, *J. Amer. Chem. Soc.*, 1932, **54**, 960; *A.*, 480; R. Luther and G. S. Forbes, *ibid.*, 1909, **31**, 770; *A.*, 1909, ii, 632.

The photolysis of hydrogen peroxide solutions, normally complex,[27] becomes simple (quantum efficiency unity) in ultra-violet light of very high intensity,[28] and by dilution with sufficient carbon tetrachloride the chain reactions in the photobromination of cinnamic acid [29] also can be suppressed to give a quantum efficiency of unity to the reaction.[30] The quantum yields of the photopolymerisation of acetylene [31] and of cyanogen [32] and of the photodecomposition of potassium persulphate solutions,[33] of ethyl diazoacetate,[34] and of chloroform,[35] and of the photobromination of benzene [36] have been measured, and observations have been made relating to the photochemical interaction of acetylene and water,[37] of carbon monoxide with ammonia and amines,[38] and of chlorine with benzene.[39]

The question of the production of formaldehyde and carbohydrates photochemically *in vitro* from solutions of carbon dioxide in water [40] has received attention, and the consensus of opinion now is that no procedure yet published enables the conditions for the reported formation of these substances to be reproduced.[41]

E. J. B.

7. FLAMES AND THE MECHANISM OF CHEMICAL CHANGE.

The subject of flames has claimed renewed attention in the past few years, and the inferences which can be drawn from the more recent lines of investigation, in particular with regard to the mechanism of chemical change, are already extensive, and promise to become more so.

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[27] F. O. Rice and M. L. Kilpatrick *J. Physical Chem.*, 1927, **31,** 1507; *A.* 1927, 1154; A. J. Allmand and D. W. G. Style, *J.*, 1930, 596, 606; *A.*, 1930, 715; M. Qureshi and M. K. Rahman, *J. Physical Chem.*, 1932, **36,** 664.

[28] L. J. Heidt, *J. Amer. Chem. Soc.*, 1932, **54,** 2840; *A.*, 918.

[29] A. Berthoud and J. Béraneck, *J. Chim. physique*, 1927, **24,** 213; *A.*, 1927, 528.

[30] W. H. Bauer and F. Daniels, *J. Amer. Chem. Soc.*, 1932, **54,** 2564; *A.*, 821.

[31] S. C. Lind and R. Livingston, *ibid.*, p. 94; *A.*, 349.

[32] T. R. Hogness and L. Ts'ai, *ibid.*, p. 123; *A.*, 349.

[33] R. H. Crist, *ibid.*, p. 3939.

[34] E. Wolf, *Z. physikal. Chem.*, 1932, [*B*], **17,** 46; *A.*, 706.

[35] D. G. Hall, *J. Amer. Chem. Soc.*, 1932, **54,** 32; *A.*, 349.

[36] E. Rabinovitsch, *Z. physikal. Chem.*, 1932, [*B*], **19,** 190.

[37] R. Livingston and C. H. Schiflett, *J. Physical Chem.*, 1932, **36,** 750.

[38] H. J. Emeléus, *Trans. Faraday Soc.*, 1932, **28,** 89; *A.*, 349.

[39] C. E. Lane and W. A. Noyes, *J. Amer. Chem. Soc.*, 1932, **54,** 161; *A.*, 349.

[40] Cf. *Ann. Reports*, 1927, **24,** 39, 225.

[41] J. Bell, *Trans. Faraday Soc.*, 1931, **27,** 771; *A.*, 29; *Nature*, 1932, **129,** 170; *A.*, 237; G. Mackinney, *J. Amer. Chem. Soc.*, 1932, **45,** 1688; F. P. Zscheile, jun., *ibid.*, p. 973; *A.*, 480; G. Mezzadroli and E. Vareton, *Atti R. Accad. Lincei*, 1931, [vi], **14,** 347; *A.*, 237; N. R. Dhar and A. Ram, *Nature*, 1932, **129,** 205; *A.*, 349, 706; M. Qureshi and S. S. Mohammad, *J. Physical Chem.*, 1932, **36,** 2205; *A.*, 1006.

Essentially, developments have occurred in three directions. First, further data and hypotheses are available concerning the more purely physical properties of flames, such as their velocities of propagation and temperatures, and the function of charged particles detected in them; whilst the conductivity of flames has been studied both experimentally and theoretically. Secondly, the investigation of the so-called "highly dilute" flames, such as are produced when alkali-metal vapours are introduced into halogens at low pressure, has led to a closer insight into certain elementary reactions between atoms and molecules. This work is highly important since modern theories of the forces between atoms and molecules make a calculation of the heats of activation of such processes *a priori* possible.[42] The manifold occurrence of "elementary processes" in gaseous chain reactions, both thermal and photochemical, has moreover made it the more desirable that they should be thoroughly understood. Thirdly, the radiation emitted from flames of various types has been examined with modern refined technique by many workers, in the infra-red and also in the visible and ultra-violet regions. Experiments on the infra-red emission offer a means of detecting any fundamental changes in the mechanism of a reaction with alteration in conditions; the example most studied in this way has been the oxidation of carbon monoxide. The examination of the visible and ultra-violet spectra has led to the detection of "flame-carriers": in particular, the occurrence of band systems indicates the existence of molecules, which, though not capable of chemical isolation, are present transitorily at least in excited states in the flames. These products are the active species essential for the continuance of the respective reactions, and can be identified with the intermediate products in chain processes. Inferences may thus be drawn about the mechanisms of those oxidation processes in which the flames have been studied in this way. There are, however, almost always unavoidable complications which make this procedure questionable, although it appears likely to become very useful in the future.

Evidence concerning the ionisation in flames and its bearing upon chemical reactions has been summarised in earlier reports.[43] F. Haber,[44] from a study of the deformation of the explosive zone and the effect on the velocity of flame propagation when gaseous explosive mixtures are passed through a wedge-shaped condenser, concludes that uncharged radicals and not electrical particles are responsible for the process of combustion and especially for the propagation of ignition. These uncharged radicals can be produced with less expenditure of energy than the charged ones, and only in the case of C–C and C–H, which have relatively low ionisation potentials, is there an appreciable splitting into ions. A. E. Malinovski and F. A. Lavrov[45] have examined the influence of an electric field on the velocity of propagation of the flame in explosive mixtures of various hydrocarbons with air, and find that the diminution in this speed which is observed in the vicinity of the region of maximum conductivity is accentuated by increase in the carbon content of the substances involved. According to these observers, this result agrees with Haber's theory, the ionisation of C–C and C–H radicals giving rise to the phenomena observed. The failure to obtain a positive effect of the field in hydrogen–oxygen mixtures was considered as substantiating evidence. W. M. Thornton,[46] on the other hand, using methane–air mixtures, finds an increase in flame speed in the electric field, and suggests an explanation based upon considerations of the internal energy of the "molecular complexes" said to be produced in the wave-front. Several series of facts are cited in support of the somewhat elaborate hypothesis, but the complications are rather serious. B. Lewis[47] has also studied this question and emphasises the importance of positive ions in the maintenance of flames. He suggests a possible explanation of the discrepancy between the results of Thornton on the one hand and of Malinovski and Lavrov on the other.

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[42] Cf. *Ann. Reports*, 1931, **28**, 19.

[43] E. K. Rideal, *ibid.*, 1928, **25**, 335; C. N. Hinshelwood, *ibid.*, 1927, **24**, 315.

[44] *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1929, **11**, 162; *A.*, 1929, 771.

H. A. Wilson[48] summarises the data and discusses the various matters relating to the electrical conductivity of flames from a theoretical standpoint.

Photographic measurements on the propagation of flame in electric fields have also been made by E. M. Guénault and R. V. Wheeler.[49] Some interesting results are described by H. F. Coward and F. J. Hartwell[50] on the uniform movement of flame in methane–air mixtures using a series of vessels differing in diameter. The maximum speed for uniform motion of the flame in a mixture of given composition is markedly decreased with decreasing vessel diameter. The relationship between the velocity *V* and diameter *D* is not simply of the type $V = cD^k$, c and k being constants, but is more complex. Several other determinations of flame speeds have been made,[51] and a new method is described by C. Becker and K. Vogt [52] employing a system of rotating mirrors.

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[45] *Z. Physik*, 1930, **59**, 690; *A.*, 1930, 424.

[46] *Phil. Mag.*, 1930, [vii], **9**, 260; *A.*, 1930, 708.

[47] *J. Amer. Chem. Soc.*, 1931, **53**, 1304; *A.*, 1931, 689.

[48] *Rev. Mod. Physics*, 1931, **3**, No. 1, 156.

[49] *J.*, 1931, 195; *A.*, 1931, 313.

[50] *J.*, 1932, 1996.

Flame temperatures form the subject of several other papers. G. W. Jones, B. Lewis, J. B. Friauf, and G. St.J. Perrott [53] have employed the spectral line reversal method to moist hydrocarbon–air mixtures, and find that the mixtures affording the maximum flame temperature contain less hydrocarbon than those affording the maximum flame speed of uniform movement. Employing the accepted values for the specific heats of carbon dioxide and hydrogen, the degrees of dissociation of carbon dioxide and of water, and the heat of dissociation of the hydrogen molecule, G. Ribaud [54] calculates the flame temperatures in burning carbon monoxide or hydrogen. Finally, P. J. Daniell [55] obtains a theoretical connexion between velocity of flame, velocity of reaction, specific heat, density, and conductivity of gaseous explosive mixtures.

" Highly diluted flames " have been mentioned previously in these Reports.[56] Summaries of the work so far carried out, with discussions of its theoretical significance, have been published by M. Polanyi [57] and G. Schay.[58] The main point in the study of these " cold " flames is that they provide a means of investigating reactions which proceed at extremely high velocity, *i.e.*, at almost every collision of the reactants without requiring heat of activation.

The view became generally accepted that atomic reactions have no inertia; in other words, in the exothermic direction they have no heat of activation. This conclusion was apparently confirmed in the reactions found to be the basis of the highly diluted flames. From measurements on the distribution of light and wall-precipitate and of the " light efficiency," under different conditions of mixing of the reactants in the long reaction tube, the mechanism of the processes occurring was elucidated. The following are examples of reactions which were found to occur at every collision and are inertia-less :

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[51] W. Payman and R. V. Wheeler, *J.*, 1932, 1835; O. C. de C. Ellis, *J. Soc. Chem. Ind.*, 1931, **50**, 403; *A.*, 1931, 1371.

[52] *Z. Physik*, 1932, **75**, 894; *A.*, 701.

[53] *J. Amer. Chem. Soc.*, 1931, **53**, 869; *A.*, 1931, 572; cf. also A. L. Loomis and G. St.J. Perrott, *B.*, 1928, 881.

[54] *Compt. rend.*, 1930, **190**, 369; *A.*, 1930, 418.

[55] *Proc. Roy. Soc.*, 1930, [*A*], **126**, 393; *A.*, 1930, 424.

[56] E. K. Rideal, *Ann. Reports*, 1928, **25**, 334; C. N. Hinshelwood, *ibid.*, 1930, **27**, 20; 1931, **28**, 47, where detailed references are given.

[57] " Atomic Reactions," London, 1932; cf. also *Naturwiss.*, 1932, **20**, 289; *A.*, 582; *Z. angew. Chem.*, 1931, **44**, 597; *A.*, 1931, 999.

[58] Hochverdünnte Flammen," *Fortschr. Chem. Physik*, 1930, **21**, 1.

$$\begin{aligned} &Na + X_2 \longrightarrow NaX + X \\ &NaX_2 + X \longrightarrow NaX + Na \\ &Na + HgCl_2 \longrightarrow NaCl + HgCl \\ &Na + HgCl \longrightarrow NaCl + Hg. \end{aligned}$$

More detailed examination of these reactions, however, and of similar ones using other substances, has now shown that many atomic processes involve a quite appreciable energy of activation. In particular, H. von Hartel and M. Polanyi [59] have found that the reactions between sodium and alkyl halides have heats of activation which increase uniformly from the iodide (about zero) to the fluoride. These experiments have been elaborately extended by H. von Hartel, N. Meer, and M. Polanyi,[60] using different alkyl radicals.

E. Horn, M. Polanyi, and H. Sattler [61] have studied the cases of sodium vapour with cadmium halides and with zinc chloride. Here the results are almost entirely similar to those originally obtained with the mercury halides, but the heats of activation are often appreciable.

The inertia-less reactions of sodium vapour with the hydrogen halides have been studied by G. Schay [62] and H. von Hartel.[63]

The calculation of heats of activation by methods arising from the results of molecular spectra and the new theories of valency have been reported elsewhere (Hinshelwood, this vol., p. 18). It is sufficient to say that the calculations lead to values which are of the same order as those observed.

A series of measurements on the total infra-red radiation emitted by the carbon monoxide–oxygen and hydrogen–oxygen flames under different conditions has been made by W. E. Garner and his collaborators.[64] In the case of hydrogen and oxygen the maximum radiation is observed with the mixture $H_2 + O_2$, and not with the stoicheiometric mixture $2H_2 + O_2$; from which the authors conclude that hydroxyl radicals are probably responsible for the emission. An examination of the effect of catalysts on the speed of the flame of carbon monoxide–oxygen mixtures, on the infra-red emission, and on the ionisation, reveals the existence of a " residual " radiation in addition to that given out in the explosion itself. Garner and Johnson suggest that this residual radiation arises from the recombination of ions. The important result with carbon monoxide flames, however, is the existence of a " step " in the curve showing total radiation emitted against percentage of hydrogen added. Addition of hydrogen diminishes the radiation observed until 0·04% is reached; at this point a break is observed, and with increasing proportion of hydrogen the radiation again diminishes, continuously, but more slowly. It should be added that, whilst diminishing the radiation produced, addition of hydrogen increases the flame speed. Garner and Roffey conclude that, in accordance with the earlier ideas of Bone, there are two chemical mechanisms operative in the reaction, one occurring below the step, the other above it. From further experiments it is concluded that excited carbon dioxide molecules are the origin of the radiation.

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[59] *Z. physikal. Chem.*, 1930, [*B*], **11**, 97; *A.*, 1930, 174.

[60] *Ibid.*, 1932, [*B*], **19**, 139. Also this vol., p. 43.

[61] *Ibid.*, 1932, [*B*], **17**, 220; *A.*, 680.

[62] *Ibid.*, 1931, [*B*], **11**, 291; *A.*, 1931, 282.

[63] *Ibid.*, p. 316; *A.*, 1931, 282.

[64] With F. Roffey, *Nature*, 1928, **121**, 56; *A.*, 1928, 105; *J.*, 1929, 1123; *A.*, 1929, 973; with C. H. Johnson, *J.*, 1928, 280; *A.*, 1928, 375; with K. Tawada, *Nature*, 1928, **122**, 879; *A.*, 1929, 21; with D. A. Hall, *J.*, 1930, 2037; *A.*, 1930, 1379; with D. A. Hall and F. E. Harvey, *J.*, 1931, 641; *A.*, 1931, 575; with K. Tawada, *Trans. Faraday Soc.*, 1930, **26**, 36; *A.*, 1930, 263; with C. E. H. Bawn, *J.*, 1932, 129; *A.*, 234; cf. also E. K. Rideal, *Ann. Reports*, 1928, **25**, 343.

Further experiments deal with the effect of vessel size, addition of inert gases, and other factors on the position and magnitude of the " step." The relationship $p_{H_2}\,p_{(CO + O_2)} = k$, originally thought to apply at this point, is later amended to $p_{H_2}\,p_{CO_2} = k$. The " step " is unaffected by changes in the vessel dimensions.

Bawn and Garner have recently stated that carbon dioxide and sulphur dioxide effect an increase of the pressure at the " step."

The visible and ultra-violet spectra emitted by flames were first examined many years ago by Kirchhoff and Bunsen. Subsequently the work was continued by Liveing, Dewar, Hartley, and others.[65] It nearly always led to the discovery of flame continua—continuous spectra, having no line or band structure.[66] The origin of such continua is still a matter of doubt; it seems probable that they arise as a result of processes of recombination of free radicals present in the flame, although alternative hypotheses are possible. In many cases, however, it is now found that superimposed upon the continua are lines or bands caused respectively by the excitation of atoms and of molecules.

All authors are agreed upon the fact that this excitation has its origin in the energy liberated in the elmentary transformations. The implications of this are twofold: first, it compels us to find in the reaction scheme some elementary process the heat evolution of which will produce the excitation observed; secondly, it enables us to infer the presence or absence of certain intermediate products in the reactions occurring.

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[65] Cf. Eder and Valenta, " Atlas typischer Spektren," 1911.

[66] Summary by W. Finkelnburg, *Physikal. Z.*, 1930, **31**, 1.

H. F. Bonhoeffer and F. Haber[67] identified the bands emitted by a hydrogen–oxygen flame with those due to hydroxyl radical, and for this and other reasons suggested that hydroxyl occurs as an intermediate product in the reaction chain. The significance of this has been discussed elsewhere.[68] It suggested the chain

$$H_2 + O_2 = 2OH,$$
$$OH + H_2 = H_2O + H,$$
$$H + O_2 + H_2 = OH + H_2O,$$

which has been so much discussed in recent years.[69]

V. Kondratéev[70] has re-examined the spectrum of the flame of burning carbon monoxide. This has been studied by W. A. Bone and his collaborators for many years.[71] Kondratéev's measurements are confined to the ultra-violet region, since in the visible, increased dispersion still leaves the spectrum too complicated for analysis. In the ultra-violet the bands are arranged in series having a frequency difference of approximately 600 $cm.^{-1}$; the corresponding infra-red and Raman frequency is 672 $cm.^{-1}$. A variety of considerations lead to the conclusion that excited carbon dioxide molecules are the emitters of the bands. The evidence is, however, to some extent negative in that the bands observed cannot be assigned to any other molecule which might be present in the flame. The change in frequency difference in the two cases could be explained by the excitation of higher vibration levels in the flame.

Kondratéev also observed the flame of sulphur burning in oxygen, the spectrum consisting of two groups of bands—one in the visible, the other in the ultra-violet—separated by a continuous region. These can be attributed to the S_2 molecule and to SO respectively. The phosphorescent flames of carbon disulphide and of ether were also studied; in the latter case formaldehyde bands are prominent.

The spectrum of the flame of carbon disulphide has been measured by A. Fowler and W. M. Vaidya.[72] It is found that the most characteristic bands of the ordinary flame, extending from the blue to the near ultra-violet, form part of the system already known to be due to S_2 molecules. The ultra-violet bands of S_2 appear in absorption but can be obtained in emission if a stream of oxygen is directed on to the flame. Emission bands of SO are seen, and if the flame is enclosed in a chimney, absorption bands of SO_2 can also be obtained.

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[67] *Z. physikal. Chem.*, 1928, **137**, [*A*], 263; *A.*, 1929, 11; cf. also *Ann. Reports*, 1928, **25**, 342; 1930, **27**, 46.

[68] W. L. Garstang and C. N. Hinshelwood, *Proc. Roy. Soc.*, 1931, **134**, [*A*], 1; *A.*, 25.

[69] W. Frankenburger, *Trans. Faraday Soc.*, 1931, **27**, 431; A., 1931, 1136.

[70] *Z. Physik*, 1930, **63**, 322; *A.*, 1930, 1332.

[71] W. A. Bone and D. T. A. Townend, "Flame and Combustion in Gases," Longmans, 1927.

[72] *Proc. Roy. Soc.*, 1931, **132**, [*A*], 310; *A.*, 1931, 996.

Generally similar results were obtained in experiments on the flames of sulphur and hydrogen sulphide, the latter showing bands of hydroxyl. The spectrum of the phosphorescent flame of carbon disulphide [73] was re-examined, and bands due to SO and CS found. Fowler and Vaidya discuss the significance of their results from the point of view of the mechanism of combustion. It is possible to reconcile all the spectroscopic data with the theory of peroxidation and with the results of kinetic measurements made on the reaction.

The spectrum of the hydrogen–nitrous oxide flame has been studied by A. Fowler and J. S. Badami.[74] These authors summarise the relevant facts concerning the most common "reference" spectra—"water vapour" bands (OH), "ammonia" bands, "third positive nitrogen" bands (NO). The results show that this flame is similar to that of ammonia burning in oxygen, each showing bands due to the molecules NH, OH, NO, and the so-called α-bands of ammonia which may be ascribed to the NH_2 molecule.

V. Kondratéev [75] has summarised the data at present available upon this subject. The following extract from his paper serves to indicate the types of result obtained :

Flame.	Molecule.	Flame.	Molecule.
$H_2 + O_2$	OH	$NH_3 + O_2$	NH, NH_2(?), OH, NO
$CO + O_2$	CO_2	$CH_4 + O_2$	CH
$S + O_2$	SO, S_2	$C_2H_2 + O_2$	CH, C_2
$CS_2 + O_2$	SO, S_2	aldehydes ethers } + O_2	C_2, CH, OH, CO_2, CH_2O
$P_4 + O_2$	PO(?)	$H_2 + N_2O$	NH, NH_2(?), OH
$(CN)_2 + O_2$	CN, C_2, CO	$CO + N_2O$	CO_2
$HCN + O_2$	CN, C_2		

H. W. T.

8. The Structure of Simple Molecules from Spectroscopic, *X*-Ray and Electron Diffraction Data.

A number of improvements in the technique of obtaining molecular spectra have been recorded, and will be found in the work referred to below; in addition may be noticed improvements in grating spectrographs [76] and far infra-red spectrographs.[77] The question of the polarisation of Raman scattering from the point of view of the " spinning photon " has received attention.[78] Accurate experimental results are difficult to obtain, and some confusion has been caused by lack of satisfactory data.

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[73] H. J. Emeléus, *J.*, 1926, 2948.

[74] *Proc. Roy. Soc.*, 1931, **133**, [*A*], 325.

[75] Proceedings of Congress on Chemical Kinetics, Leningrad, Sept. 1930.

[76] A. L. Loomis and G. B. Kistiakowsky, *Rev. Sci. Instr.*, 1932, [ii], **3**, 201; *A.*, 592.

[77] H. M. Randall, *ibid.*, p. 196; *A.*, 592; R. B. Barnes, *Physical Rev.*, 1932, [ii], **39**, 562; *A.*, 444.

An outline of the methods by which the structure of a simple molecule can be deduced has already been given.[79] From *X*-ray or electron-diffraction methods intramolecular distances are obtained.[80] The fine-structure, *i.e.*, the rotational constituent, of absorption bands in the infra-red, visible, or ultra-violet region, or of Raman bands [81] provides values of the moments of inertia of the molecule, whence the interatomic distances and angles can be calculated. The vibrational frequencies of the molecule, also obtained from absorption band or Raman data, through a treatment of the molecule as a system of masses and springs, allow of calculations of the angular dispositions of the masses and of the force constants of the links.[82] The spectroscopic methods naturally depend for their reliability on the accuracy of the interpretation of the experimental data, that is, on the correct allocation of observed frequencies to particular transitions. This would not be so difficult if every important vibrational band were completely resolved into its rotational constituents and selection rules applied.[83] Owing, however, to the elaborate technique necessary to overcome the experimental difficulties, there is at present a lack of adequate data for most simple molecules, so that the selection of moments of inertia, and still more, of fundamental vibrational frequencies, often becomes a debatable rather than an answerable problem. Further difficulties arise in the question of the distribution of forces within the molecule, *i.e.*, whether the forces are associated only with chemical linkages, and whether repulsions between non-linked atoms occur.[84] It is towards the solution of these difficulties that most of the work on the structure of simple molecules is at present directed.

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[78] (Sir) C. V. Raman and S. Bhagavantam, *Indian J. Physics*, 1931 **6,** 353; *A.*, 107; *Nature*, 1932, **129,** 22; S. Bhagavantam, *Indian J. Physics*, 1932, **7,** 79; *A.*, 793; *Nature*, 1932, **129,** 167; R. Bär, *ibid.*, p. 505; *A.*, 445; S. Bhagavantam and S. Venkateswaran, *ibid.*, p. 580; *A.*, 445; S. Venkateswaran, *Phil. Mag.*, 1932, [vii], **14,** 258; *A.*, 898; J. Cabannes and A. Rousset, *Compt. rend.*, 1932, **194,** 79, 706; *A.*, 212, 320.

[79] *Ann. Reports*, 1931, **28,** 367. Note: in the formulæ on p. 371 the units are not accurately defined, and reference should be made to K. W. F. Kohlrausch, " Der Smekal-Raman Effekt," Springer, Berlin, 1931.

[80] H. Gajewski, *Physikal. Z.*, 1932, **33,** 122; *A.*, 316; R. W. James, *ibid.*, p. 737; W. van der Grinten, *ibid.*, p. 769.

[81] For rotational structure of Raman bands, see K. W. F. Kohlrausch, *op. cit.*, p. 50; A. Langseth, *Z. Physik*, 1931, **72,** 350; A. Carrelli and J. J. Went, *ibid.*, 1932, **76,** 236; *A.*, 792.

[82] See R. Mecke, *Z. physikal. Chem.*, 1932, [*B*], **16,** 409, 421; **17,** 1; *A.*, 559, 675.

[83] G. Placzek, *Z. Physik*, 1931, **70,** 84; *A.*, 1931, 893; D. M. Dennison, *Rev. Mod. Physics*, 1931, **3,** 289; H. A. Kraus and G. P. Ittmann, *Z. Physik*, 1930, **60,** 663.

As an illustration of the methods employed in correlating infra-red absorption-band data with Raman frequencies in order to obtain the energy levels of the molecule, reference may be made to A. Langseth and J. R. Nielsen,[85] to P. E. Martin and E. F. Barker,[86] and to D. M. Dennison,[87] who examine the case of the molecule of carbon dioxide.[88] This molecule definitely has a linear symmetrical structure.[89] The molecule of nitrous oxide is more complicated and, though linear, has the unsymmetrical structure NNO.[90] This structure is also supported by other evidence of a very varied character,[91] though it is not at present easy to reconcile this result with the very small dipole moment of the molecule.[92]

The structure of the H_2O molecule in the light of refined near infra-red absorption band measurements has been discussed by P. Lueg and K. Hedfeld,[93] who conclude (from the calculated moments of inertia) that the molecule is an isosceles triangle of the following dimensions: O—H = 0·98 Å.; H—H = 1·6 Å.; angle HOH = 109°. In this paper full references to earlier work will be found. Other new data for this molecule are presented by E. K. Plyler,[94] L. R. Weber and H. M. Randall,[95] S. Rafalowski,[96] H. Hulubei,[97] and H. Gajewski.[98]

Hydrogen sulphide appears to be a rectangular isosceles triangle with S—H = 1·43 Å. and H—H = 2·02 Å.[99] A. Dadieu and K. W. F. Kohlrausch [99] from a general survey conclude that the OSO angle in sulphur dioxide is 120°. C. R. Bailey and A. B. D.

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[84] H. C. Urey and C. A. Bradley, *Physical Rev.*, 1931, [ii], **38**, 1969; *A.*, 107.

[85] *Z. physikal. Chem.*, 1932, [*B*], **19**, 35.

[86] *Physical Rev.*, 1932, [ii], **41**, 291.

[87] *Ibid.*, p. 304; *A.*, 982.

[88] See also A. B. D. Cassie and C. R. Bailey, *Z. Physik*, 1932, **79**, 35.

[89] For *X*-ray results, see H. Gajewski, *loc. cit.* (ref. 80).

[90] E. K. Plyler and E. F. Barker, *Physical Rev.*, 1931, [ii], **38**, 1827; *A.*, 1931, 108; A. Langseth and J. R. Nielsen, *Nature*, 1932, **130**, 92; *A.*, 897.

[91] K. Clusius, *Nature*, 1932, **130**, 775; G. Herzberg, *Z. physikal. Chem.*, 1932, [*B*], **17**, 68; *A.*, 680; C. R. Bailey, *Nature*, 1932, **130**, 239; *A.*, 997.

[92] H. v. Braunmühl, *Physikal. Z.*, 1927, **28**, 141; J. W. Williams and C. H. Schwingel, *Physical Rev.*, 1930, [ii], **35**, 855; P. C. Mahanti, *Physikal. Z.*, 1931, **32**, 108; *A.*, 1931, 287.

[93] *Z. Physik*, 1932, **75**, 512; *A.*, 558.

[94] *Physical Rev.*, 1932, [ii], **39**, 77; *A.*, 212.

[95] *Ibid.*, **40**, 835; *A.*, 792 (far infra-red).

[96] *Bull. Acad. Polonaise*, 1931, [*A*], 623; *A.*, 792.

[97] *Compt. rend.*, 1932, **194**, 1474; *A.*, 559 (Raman spectra).

[98] *Loc. cit.* (ref. 80).

[99] A. Dadieu and K. W. F. Kohlrausch, *Physikal. Z.*, 1932, **33**, 165; *A.*, 320.

Cassie[1] from infra-red data show that there is a close similarity of structure between sulphur dioxide and chlorine dioxide. The unpaired electron of the latter therefore takes no part in the linkages of the molecule. According to the assumptions made as to the distribution of forces within the molecule, they show that two structures can be deduced, the angles OSO and OClO being 60° for "central forces" and 122° and 140° respectively for "valence forces." On evidence based on the as yet incompletely resolved rotational structure they prefer the smaller angle, as the larger appears to give too great interatomic distances.[2] The chemist, however, would select the larger-angled solutions as having valency forces and agreeing with the selection rules, and would regard the question of the linear dimensions of the molecules as still unsettled.

Chlorine monoxide is probably a rectangular isosceles triangle.[3] The ozone molecule is reported on Raman spectra evidence to be triangular but not equilateral;[4] its structure may possibly be analogous to that of sulphur dioxide.

The vibrational structure of the near infra-red absorption bands[5] and of the Raman bands[6] of ammonia has been carefully investigated, but entire agreement has not yet been reached as to the moments of inertia of the molecule. One of them is difficult to obtain from spectroscopic data, but can be calculated by an application of wave-mechanics.[7] The original pyramidal form[8] has been confirmed, but the table below shows the structures deduced by different treatments of the experimental data:

Distances (Å.) and angles.	Lueg and Hedfeld.	Dennison and Uhlenbeck.	Langseth. (Gaseous.)	(Dissolved in water.)
N—H	1·04	1·02	0·89	0·90
H—H	1·72	1·64	0·92	0·93
Height of pyramid	0·3		0·71	0·73
Angle HNH	110°	107°	62°	62°

The HNH angle of about 110° is probably the most reliable; Langseth's results depend on the choice of a very small value for one of the moments of inertia, but independently of the probable inaccuracy of this choice they serve to show how little the ammonia molecule is deformed by dissolution in water.

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[1] *Nature*, 1932, **129**, 652; *A.*, 888; *Proc. Roy. Soc.*, 1932, [*A*], **137**, 622; *A.*, 1075.

[2] Cf. R. Wierl, *Physikal. Z.*, 1930, **31**, 1028; *A.*, 1931, 13.

[3] C. R. Bailey and A. B. D. Cassie, *loc. cit.* (ref. 1).

[4] G. B. B. Sutherland and S. L. Gerhard, *Nature*, 1932, **130**, 241; *A.*, 983.

[5] P. Lueg and K. Hedfeld, *Z. Physik*, 1932, **75**, 599; *A.*, 674.

[6] A. Langseth, *ibid.*, **77**, 60; *A.*, 897; E. Amaldi and G. Placzek, *Naturwiss.* 1932, **20**, 521; *A.*, 897.

[7] D. M. Dennison and G. E. Uhlenbeck, *Physical Rev.*, 1932, [ii], **41**, 313; *A.*, 982; N. Rosen and P. M. Morse, *ibid.*, **42**, 210.

[8] R. M. Badger and R. Mecke, *Z. physikal. Chem.*, 1929, [*B*], **5**, 333; *A.*, 1929, 1363.

Pentatomic tetrahedral molecules have been examined by a number of workers. J. G. Moorhead[9] has calculated moments of inertia of the methane molecule, and a discussion of the fundamental frequencies of the molecule is given by S. Bhagavantam.[10] C. Schaefer and R. Kern[11] present accurate measurements of the infra-red absorption bands of carbon tetrachloride and attempt to allocate the bands to particular transitions in terms of the four fundamental frequencies.[12] H. C. Urey and C. A. Bradley[13] show that the four fundamental frequencies of the tetrahedral molecules CCl_4, $SiCl_4$, $SnCl_4$, CBr_4, $SnBr_4$, and $TiCl_4$ cannot be related to one another on the simple assumption of valency forces; an allowance must be made in addition for the mutual repulsion of the corner atoms.

New infra-red absorption bands of formaldehyde vapour have been measured,[14] and G. Herzberg and K. Franz[15] find that the molecule gives a fluorescence spectrum with two characteristic frequency differences identical with the Raman lines. From the rotational structure of the ultra-violet absorption spectrum, G. H. Dieke and G. B. Kistiakowsky[16] deduce the distances: C—O = 1·19 Å.; H—H = 1·88 Å.; C—H = 1·15 Å.; angle HCH = 110°.

The identification of the vibrations of the acetylene molecule are at present uncertain;[17] provisional moments of inertia for the ethylene molecule have been arrived at by R. M. Badger and J. L. Binder.[18]

It is remarkable that the angles obtained between the valencies of the hydrogen atoms in the molecules H_2O, H_3N, (H_4C), and H_2CO are all close to the tetrahedral angle 109° 28′; H_2S at present appears to be an exception with an angle of 90°. E. J. B.

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[9] *Physical Rev.*, 1932, [ii], **39**, 83; *A.*, 212.

[10] *Nature*, 1932, **129**, 830; *A.*, 675.

[11] *Z. Physik*, 1932, **78**, 609.

[12] Cf. A. Langseth, *ibid.*, 1931, **72**, 350; *A.*, 1931, 1363.

[13] *Physical Rev.*, 1931, [ii], **38**, 1969; *A.*, 107.

[14] J. R. Patty and H. H. Nielsen, *Physical Rev.*, 1932, [ii], **39**, 957; *A.*, 558; R. Titeica, *Compt. rend.*, 1932, **195**, 307; *A.*, 897.

[15] *Z. Physik*, 1932, **76**, 710; *A.*, 896.

[16] *Proc. Nat. Acad. Sci.*, 1932, **18**, 367.

[17] A. R. Olson and H. A. Kramers, *J. Amer. Chem. Soc.*, 1932, **54**, 136; *A.*, 320; W. Lochte-Holtgreven and E. Eastwood, *Nature*, 1932, **130**, 403; *A.*, 1075.

[18] *Physical Rev.*, 1931, [ii], **38**, 1442; *A.*, 6; see also H. H. Nielsen, *ibid.*, p. 1432; *A.*, 6.

9. GENERAL STEREOCHEMISTRY.

During this year the greater part of the new and comprehensive textbook of Stereochemistry edited by K. Freudenberg[19] has appeared. The earlier parts contain very thorough discussions of the physical aspects of the subject, by Mark, V. M. Goldschmidt, Mecke, Dadieu, and others, including a discussion of the new physical theory of optical activity by Werner Kuhn. The more organic side is discussed in the later parts, by Freudenberg, Ebel, Richard Kuhn, Meisenheimer, and others. This book brings together for the first time the various physical and chemical investigations bearing on the subject.

W. H. Mills has published two important papers dealing with general aspects of stereochemistry. In the first[20] he discusses the energy relations of the cyclic compounds and the conditions of their formation. In the second[21] he deals especially with the mechanism of the racemisation of tercovalent atoms, and of the transmigration in the Beckmann reaction; he also gives the clearest and most thorough discussion which has yet appeared of the origin of optically active compounds in living matter, and shows how the growth of an organism must necessarily accentuate any disproportion between the antimeric forms.

Now that the normal arrangements of the valencies of multivalent atoms have been ascertained, we are in a position to consider what modifications the molecule can undergo, how far it resists these modifications, and what are the forces that tend to bring them about.

The modifications are of three kinds :

(I) Rotation of atoms with their attached groups about the line of a single link : " free rotation."

(II) Bending of the valencies, *i.e.*, expansion or contraction of their angles.

(III) Stretching or compression of the links : increase or diminution of the distances between the linked atoms.

The restoring forces exerted by the valency bonds themselves against these deformations are for (I) zero, since no change of angle or distance is involved.

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[19] " Stereochemie : eine Zusammenfassung der Ergebnisse, Grundlagen und Probleme," Leipzig, Deuticke, 1932; 5 of the 8 parts have now been published, price RM. 18 each.

[20] Stéréochimie des composés cycliques : Report of the Fourth Chemical Solvay Conference, Paris, Gauthier-Villars, 1931, pp. 1—51.

[21] Presidential Address to the Chemical Section of the British Association : in " The Advancement of Science," 1932, pp. 37—56. *B. A. Report*, 1932, p. 37.

For (II) they are given by the force constants derived from the absorption or Raman spectra. These are much less easy to determine for the bending than for the stretching, and are only known in a few simple instances. For the C–H link the Raman spectra indicate[22] that a change of angle of 10° (about 0·1 Å.U.) requires about 700 cals. per g.-mol. : for the linear molecule of hydrogen cyanide and acetylene the spectrum gives[23] similar values of 788 and 772 cals. respectively. We may assume that this resistance is much the same for other atoms attached to carbon. As will be shown later, there is reason to think that for the valencies of oxygen and sulphur, and perhaps of all atoms with a covalency of less than four, it is very much smaller.

(III) The resistance to stretching is much greater, and is given by the force constants, which are known for a large number of links.[24] The energy required for an increase of distance of 0·1 Å.U. is on the average 3000 cals. for a single link; for C–Cl it is 2200 cals.[23]

The agencies external to the valencies which tend to deform the molecules are :

1. The thermal impacts of other molecules : energy = kT, or 600 cals. per g.-mol. at 25°.

2. The dipole attractions and repulsions;[25] for two dipoles of moment 1×10^{-18} e.s.u. at a distance of 3 Å.U., the dipole potential —the work of complete separation of the dipoles—is about equal to the thermal energy at 25°.

3. The van der Waals attraction between the atoms.[26] The importance of this factor has only recently been recognised, and is still somewhat doubtful. It seems, however, to be effective in ethylene dichloride, according to the recent observations of Kohlrausch. The scattering of X-rays by the vapour of ethylene dichloride showed[27] that the majority of the molecules had the chlorine atoms as far removed as possible (" *trans*-position "), but the shape of the curves indicated that not all the molecules were in this state. It was concluded that the *trans*- was the favoured position, owing to the dipole repulsion, but that the thermal agitation, which for this molecule should be of the same order of magnitude as the dipole potential, disturbed the molecules from it

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[22] See *Ann. Reports*, 1931, **28**, 371, 401.

[23] H. A. Stuart, *Physikal. Z.*, 1931, **32**, 793; *A.*, 1931, 1356.

[24] *Ann. Reports*, 1931, **28**, 401.

[25] *Ibid.*, p. 390.

[26] For a detailed discussion, based on wave mechanics, of this and the other intermolecular and interatomic forces, see H. Eyring, *J. Amer. Chem. Soc.*, 1932, **54**, 3191; *A.*, 996.

[27] P. Debye, *Physikal. Z.*, 1930, **31**, 142, 419; *A.*, 1930, 400, 843 : observed distance, 4·4 ± 0·1 Å.U. : calculated for *trans*-form, 4·25.

to some extent. This was confirmed by the measurement of the dipole moment, which was found to be considerable, though less than that required for the *cis*-form (the *trans*- has no moment), and to increase with rise of temperature owing to the greater freedom of rotation;[28] it was also found that in solution, where the dielectric constant of the medium is larger, and hence the dipole potential smaller, the moment is larger than it is in the gas. It has now, however, been shown[29] that in the Raman spectrum of ethylene dichloride the line corresponding to the oscillations of the C–Cl link is double, one component being stronger than the other, and the ratio of the intensities approaching unity as the temperature rises. In *cis*- and *trans*-dibromoethylene, which are distinct substances, the C–Br Raman lines are not quite in the same position, indicating that the constant for the C–Br link is somewhat different according as the second C–Br link is in the *cis*- or *trans*-position.[30] Kohlrausch concludes from this that ethylene dichloride consists, not of molecules in or near the *trans*-position, but of a definite mixture of the *cis*- and the *trans*-form, with the latter predominating; otherwise we should find one blurred line instead of two sharp ones. If so, there must be some force to hold the molecule for a time in the *cis*-position, against the dipole repulsion, and this can only be the van der Waals attraction of the chlorine atoms, which in the *cis*-position are about 2·7 Å.U. apart, much like neighbouring molecules of liquid or solid chlorine. The work required to separate them against this force can be roughly estimated from the heat of evaporation of chlorine. This is, at the ordinary temperature, about 4 kg.-cals. per g.-mol., or 2 kg.-cals. per g.-atom. If we suppose that in the evaporation of the liquid each chlorine atom has to overcome the van der Waals attraction of 4 or 5 neighbours, this would make the heat of separation of two atoms 400—500 cals., which is of the same order as the dipole potential. The same influence seems to be active in dichloroethylene, $CHCl{:}CHCl$. Here the *cis*- and the *trans*-form (b. p. 60·1° and 47·5°) are stable at the ordinary temperature, but change into one another at measurable rates in the vapour at 300°; and it has been found[31] that the equilibrium mixture, from whichever side it is approached, contains about 63% *cis* and 37% *trans*. Since the dipole repulsion must certainly favour the *trans*-configuration, we can only conclude that the van der Waals force is more effective in the opposite direction.

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[28] C. P. Smyth, R. W. Dornte, and E. B. Wilson, *J. Amer. Chem. Soc.*, 1931, **53**, 2005, 4242; *A.*, 1931, 786; 1932, 110; C. T. Zahn, *Physical Rev.*, 1931, [ii], **38**, 521; *A.*, 1931, 1113.

[29] K. W. F. Kohlrausch, *Z. physikal. Chem.*, 1932, [*B*], **18**, 61; *A.*, 897.

[30] A. Dadieu, A. Pongratz, and K. W. F. Kohlrausch, *Monatsh.*, 1932, **60**, 221; *A.*, 898.

[31] L. Ebert and R. Büll, *Z. physikal. Chem.*, 1931, [*A*], **152**, 451; *A.*, 1931, 430. For a discussion, see H. A. Stuart, *Physikal. Z.*, 1931, **32**, 793; *A.*, 1931, 1356.

4. Electron repulsion of non-linked atoms. The " atomic radii " calculated from the distances between the nuclei of linked atoms are now known to within a few hundredths of an Å.U. But the least distance between two atoms which are not linked is much greater than corresponds to these radii; and this fact, which is of great importance in stereochemical phenomena, has been somewhat overlooked. For example, the " radius " of a krypton atom can be determined (1) from its spectrum, giving a value corresponding to the radius in a link, the " internal " radius; (2) from the viscosity of the gas,[32] the " collision radius "; (3) from the crystalline solid. The values are: spectroscopic 1·06, collision radius 1·55, crystal radius 2·01 Å.U. This shows that the distance of nearest approach is in the crystal about 2 Å.U. and in the gas about 1 Å.U. greater than in the link. For this greater distance in the crystal there is much evidence. The densities of the diatomic " permanent " gases in the solid state, compared with those deduced from their internal radii, show that to fill up the space in the crystal we must put an " envelope " about 1 Å.U. thick round each molecule. In solid benzene hexachloride the minimum distance between the nuclei of two chlorines belonging to different molecules is 3·74 Å.U.[33] This gives an external radius of 1·87, and if we subtract the internal radius of 0·97 Å.U., we are left with an envelope 0·90 Å.U. thick. So, too, Hendricks [34] has shown that in a whole series of solid organic compounds the nearest approach of two carbon atoms of different molecules is from 3·6 to 3·9 Å.U. In graphite the distance between the separate flat sheets, each of which is really a giant molecule, is 3·41 Å.U. These distances are due essentially to the electrostatic repulsion of the electrons, whose magnetic moments are already paired within the molecule. This force will gradually increase as the atoms approach one another, until it balances the van der Waals attraction, which is due to polarisation and resonance.

The chemist is more interested in molecules in the liquid or gaseous than in the solid state, and here owing to their greater freedom of motion they will come nearer, and the " envelopes " will be thinner, as the collision radii show. The data for liquids and vapours are less direct than for solids, and the distances will obviously vary with the conditions, and especially with the thermal energy.

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[32] For a very ingenious method of deducing the structure from the collision area, see R. M. Melaven and E. Mack, *J. Amer. Chem. Soc.*, 1932, **54**, 888; E. H. Sperry and E. Mack, *ibid.*, p. 904; E. Mack, *ibid.*, p. 2141; *A.*, 563, 566, 904.

[33] S. B. Hendricks and C. Bilicke, *ibid.*, 1926, **48**, 3007; *A.*, 1927, 98.

[34] *Chem. Reviews*, 1930, No. 4.

Good evidence of this repulsion is given by the measurements, from the scattering of X-rays by the vapour,[35] of the distances between the chlorine atoms in carbon tetrachloride, chloroform, and methylene chloride, which present several points of interest. As successive chlorine atoms are replaced by hydrogen atoms, this distance steadily increases :

CCl_4 : Cl–Cl, 2·99 ± 0·03 Å.U.
$CHCl_3$: ,, 3·11 ± 0·05 Å.U.
CH_2Cl_2 : ,, 3·23 ± 0·1 Å.U.

In carbon tetrachloride the absence of dipole moment and the spectroscopic data indicate that the molecule is symmetrical and hence the valency angle is 109° 28′ ; the C–Cl distance must therefore be 1·83 ± 0·02 Å.U. The distance between carbon and chlorine in methyl chloride is given [35] as 1·9 ± 0·1 Å.U., but for a molecule of this kind the calculation of the distance from the curves is peculiarly difficult, and the result may be in error by as much as 0·2 or 0·3 Å.U. The "internal" radius of carbon is known from many sources to be 0·77, and that of chlorine, as measured in the gas, and confirmed by many of its compounds, is 0·97, giving the C–Cl distance as 1·74 Å.U. This is compatible with the results obtained for methyl chloride, but in carbon tetrachloride, where the measurements are much more accurate, the distance is found to be nearly 0·1 Å.U. longer. Now, if in carbon tetrachloride the chlorine atoms are crushed together against their mutual repulsion, this must lead to a stretching of the link between them, and the observed excess of 0·09 A.U. in their distance may well be due to this cause. It can be shown that an extension of this order is to be expected. The potential energy due to the whole distortion in the carbon tetrachloride molecule, the crushing and the stretching (there is no bending) can be found from the observed heat of formation. The heat of formation from its atoms of the C–Cl link is 74·7 kg.-cals. in methyl chloride, and 77·6 kg.-cals. in ethyl chloride. We may take the mean value 76·2 as the heat of formation of the unstrained C–Cl link. Hence that of the carbon tetrachloride molecule, if there were no strain, would be 4 × 76·2 = 304·8 kg.-cals. The observed value is 290·4 kg.-cals., and the difference, 14·4 kg.-cals., must represent the potential energy of the strain in the molecule in all its forms. From the force constant for C–Cl quoted above we can calculate that to stretch the C–Cl link by 0·09 Å.U. needs 1·8 kg.-cals., or for the four links 7·2 kg.-cals. This leaves 14·4 — 7·2

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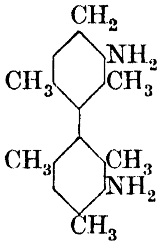
[35] P. Debye, *Z. Elektrochem.*, 1930, **36**, 612; *A.*, 1930, 1350.

= 7·2 kg.-cals. for the potential energy of compression of the chlorine atoms. The data used in this calculation, especially the thermal data, are only approximate, and errors of 2 or 3 kg.-cals. are quite possible; but the results are sufficient to show that the energy relations are of the right order.

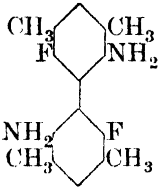
This question of the length of the link is important when we try to calculate the valency angles in chloroform and methylene chloride. If we take the length of the C–Cl link to be 1·83 Å.U., the Cl·C·Cl angle in methylene chloride is 124° ± 6° : if we take it to be 1·74 Å.U. the angle is 136° ± 6°. In either case it appears that the mutual repulsion of the chlorine atoms is sufficient to separate them, against the resistance which the valencies offer to bending, to a distance of 3·2 Å.U., which involves an " envelope " rather more than 0·6 Å.U. thick. It is, of course, to this atomic repulsion that the " Thorpe–Ingold " effect is due.

Another problem connected with atomic repulsion is that of the optical activity of ortho-substituted diphenyl derivatives.[36] The suggestion of Mills and Kenyon that this is due to a steric interference of the ortho-groups, preventing the rotation of one nucleus round the common axis of the two, has been fully confirmed by the work of W. H. Mills and K. A. C. Elliott,[37] who found the same phenomenon with a 1 : 8-naphthalene derivative; and recently Mills and J. G. Breckenridge [38] have shown that it occurs also with 8-substituted *N*-alkylquinolines. Various attempts [39] have been made to determine what are the smallest groups or atoms which in the ortho-position can inhibit the rotation. It was found that with four ortho-methyl groups (I) racemisation practically does not occur;[40] and that with fluorine and NH$_2$ on each ring [41] (II) the racemisation, though easy, is not instantaneous : it needs about

(I.)



(II.)



[36] For earlier references, see *Ann. Reports*, 1926, **23**, 119; 1931, **28**, 394.

[37] *J.*, 1928, 1291.

[38] *J.*, 1932, 2209.

[39] See *e.g.*, R. Adams and co-workers, *J. Amer. Chem. Soc.*, 1929—32 : E. E. Turner and co-workers, *J.*, 1929—32.

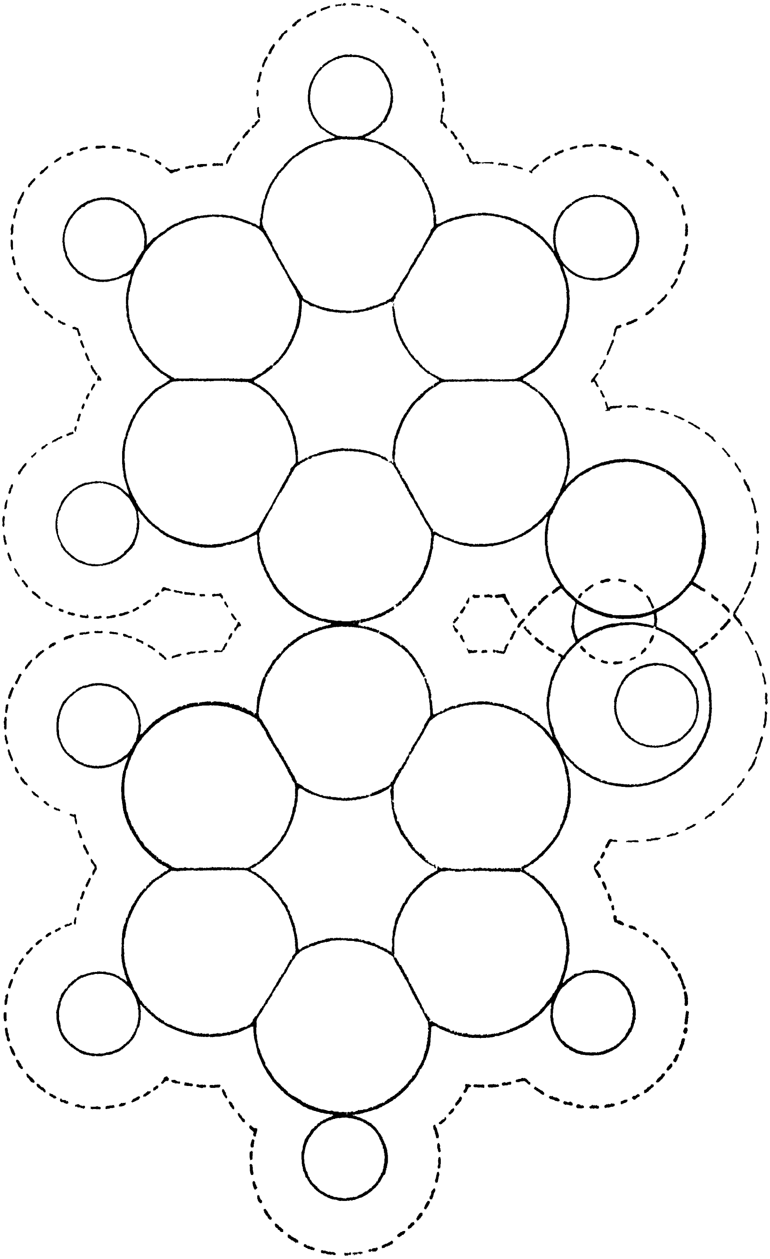
[40] W. W. Moyer and R. Adams, *J. Amer. Chem. Soc.*, 1929, **51**, 630; *A.*, 1929, 437.

[41] E. C. Kleiderer and R. Adams, *ibid.*, 1931, **53**, 1575; *A.*, 1931, 720.

20 minutes in boiling ethyl alcohol. These last are the smallest groups which have yet been found capable of preventing racemisation. A model of *o*-fluoro-*o′*-aminodiphenyl is given in Fig. 3; the radii adopted are: C 0·77 (C–C in the ring 1·42), N 0·71, F 0·68, H 0·37. It will be seen that if the hydrogen atoms of the amino-group are turned out of the way, the "inner spheres" of the nitrogen and fluorine atoms do not touch. The geometry of the ortho-positions in diphenyl is very simple; if R is the radius of the atoms attached to the *o*- and *o′*-carbons, the nuclei of these atoms will be $2{\cdot}19 - R$ Å.U. apart; hence their inner spheres will be $2{\cdot}19 - 3R$ apart, and will touch if R is greater than $2{\cdot}19 \div 3$, or 0·73 Å.U. The radii of fluorine and nitrogen are just below this limit, and it is impossible to explain, if we take account only of the inner spheres, why these two atoms should restrict rotation. But if we admit that the repulsion extends beyond this range, we can see that it may be effective, as is shown in the diagram, where the dotted line represents an envelope 0·5 Å.U. thick. It will be observed that the envelopes of the unsubstituted hydrogen atoms on the left-hand side of the diagram are not more than about 0·1 Å.U. apart.

The question of the racemisation of the diphenyl derivatives is very different from that presented by the chlorinated methanes, in that it is dynamic and not static. It is impossible to detect the optical activity of a compound if its time of half racemisation is much less than one minute. Hence an effective steric hindrance is one which requires more energy to overcome it than that of the heaviest blow which the molecule receives in a minute. A molecule of a diphenyl derivative in dilute solution at 25° will make about 10^{13} collisions a second with the solvent, the average energy of the collisions being 600 cals. per g.-mol. The number of collisions of higher energy than the mean can be calculated by Boltzmann's equation, which shows, *e.g.*, that there will be one collision of 30 times the mean energy (18,000 cals.) about every ten seconds. Only some of these collisions will tend to turn the molecule round and cause racemisation; we may perhaps assume that 10% will be effective. In that event, if the work required to overcome the resistance of the envelope—the heat of activation—is 18,000 cals., the molecule will on the average be racemised in 100 seconds, which means that its activity will last just long enough to be detected. This conclusion is confirmed by the observation of Mills and Elliott that their 1 : 8-naphthalene derivative, which racemised with a half life of 16 minutes in chloroform at 15°, had a heat of activation, as determined from the temperature coefficient of the velocity of racemisation, of 18,500 cals.

FIG. 3.



Scale 148 *Millions* : 1 (1 Å.U. = 1·48 *cms.*)

Another group of phenomena in which the atomic repulsion seems to be concerned is the valency angles as measured by means of the dipole moments.[42] This work has led to the remarkable conclusion that while the angle for carbon is not much greater than the tetrahedral (110—120°), for oxygen and sulphur it is far larger, and usually about 140°; although, according to the wave-mechanical conclusions of Pauling, the angle for oxygen and sulphur should be nearer to 90°. This can only be understood by considering the actual compounds employed. In order to avoid complications due to the mutual induction of dipoles, it is desirable to have these removed in the molecule as far as possible from one another. Hence the method usually adopted is to compare the moment of diphenylmethane, or diphenyl ether or thioether, with those of its mono- and di-substitution products containing polar groups (CH_3, Br, NO_2) in the para-position. What we really learn, therefore, is the angle of the valencies attaching carbon, oxygen, or sulphur to two phenyl groups.

It is easy to see from the model that if the two rings are to be capable of rotating independently of one another, and so of passing through a plane phase, the valency angle of the central carbon or oxygen must be rather larger than the tetrahedral angle (about 118°) even if we disregard the envelopes of the hydrogen atoms in the ortho-positions; if we take these into account it will be about 140°. In the dipole measurements we are concerned with the average value of the valency angle, and not with the result of exceptionally severe blows. There is of course no necessity for the two rings to have the plane structure as one of their normal phases, but it is obvious that the thermal agitation will tend to promote this, and will increase the valency angle to some extent. The extent will depend on the resistance of the angle to deformation, of which we know the value for carbon, but not for any other element. Taking the energy of bending of the carbon valencies as 750 cals. for 10°, we can see that if the whole 600 cals. of energy of the thermal impacts was devoted to increasing this angle (which of course is impossible), it would cause an expansion of 9°. The dipole measurements indicate that for carbon the expansion is not more than 10° at the outside, but for oxygen and sulphur it is about 30° (if we accept Pauling's view that the normal angle for a bicovalent atom is a right angle, it is 50°). This strongly suggests that the resistance to bending of the valencies of a bicovalent atom is far weaker than with an element in which all the 8 electrons of the octet are shared; indeed, since the energy is proportional to the square of the deflexion, it suggests that the value for oxygen or sulphur is not more than a thirtieth of that for carbon—say 30 cals. for 10° instead of 750. The Raman data for compounds like water should afford evidence on this point, but it does not seem that this has yet been obtained.

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[42] E. Bergmann and co-workers, *Z. physikal. Chem.*, 1930, [*B*], **8**, 111; *A.*, 1930, 979; [*B*], **10**, 397; *A.*, 1931, 23; 1932, [*B*], **17**, 81, 92, 100, 107; *A.*, 677; *Ber.*, 1932, **65**, 446, 457; *A.*, 506, 507; *Z. Elektrochem.*, 1931, **37**, 563; O. Hassel and E. Næshagen, *Z. physikal. Chem.*, 1932, [*B*], **15**, 417; *A.*, 322; K. L. Wolf, *ibid.*, [*B*], **17**, 465; *A.*, 794; C. P. Smyth and W. S. Walls, *J. Amer. Chem. Soc.*, 1932, **54**, 1854, 3230; *A.*, 794, 984.

This conclusion seems to be supported by the heats of formation of multiple links.[43] It has been found that the relative values of the heats of formation from their atoms of single, double, and triple links of carbon to carbon are as 1 : 1·8 : 2·3, which is an indication of the strain in the multiple links; but that for the links of carbon to nitrogen, oxygen, or sulphur the values are almost exactly as 1 : 2 : 3, which shows that with these elements the strain is much less.

N. V. S.

E. J. Bowen
C. N. Hinshelwood
N. V. Sidgwick
H. W. Thompson
J. H. Wolfenden

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[43] *Ann. Reports*, 1931, **28**, 387.

INORGANIC CHEMISTRY.

In reviewing the work on Inorganic Chemistry which has been published during the past year it is perhaps allowable in the first place to take a somewhat wider view and to consider the main lines upon which investigations have run during the past few years.

I. *Discovery and Investigation of New Elements.*

This phase of chemistry has, of course, almost come to an end. Nevertheless, a great deal of work has been done on the compounds of the element rhenium, which was only discovered as recently as 1925.[1] Masurium,[2] announced at the same time as rhenium and illinium (At. No. 61), seems to have gone the same way as so many new elements, but the search for these and for the missing alkali metal (No. 87) and halogen (No. 85) is being prosecuted with the aid of all the modern technique and appliances.[3] There is a tendency to name these elements somewhat prematurely. It has been suggested that the highest possible atomic number is 92.[4]

II. *Investigation of Compounds of the Rarer Elements.*

Richer sources and improved methods of extraction of rarer elements, as well as the discovery of technical applications of many of them, have been responsible for a greatly increased interest in such elements as rubidium and cæsium,[5] beryllium,[6] gallium,[7] and germanium.[7]

III. *Striking Developments with Old Elements.*

Applications of modern theories and refined physical methods have shown that there is still much to discover about some of the best known elements. The separation of ortho- and para-hydrogen may be cited as a case in point,[8] and also the discovery of isotopes of hydrogen,[9] carbon,[10] nitrogen,[10] and oxygen,[10] which until quite recently had been regarded as simple elements.

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[1] *Ann. Reports*, 1928, **25**, 59; 1929, **26**, 65; 1930, **27**, 73; 1931, **28**, 59; this vol., p. 88.

[2] *Ibid.*, 1925, **22**, 63.

[3] *Ibid.*, 1929, **26**, 43; 1931, **28**, 49; F. Allison and E. J. Murphy, *Physical Rev.*, 1930, [ii], **35**, 285; *A.*, 1931, 1391; J. L. McGhee and M. Lawrenz, *J. Amer. Chem. Soc.*, 1932, **54**, 405; *A.*, 355; F. Allison, E. R. Bishop, A. L. Sommer, and J. H. Christensen, *ibid.*, p. 613; *A.*, 317; F. Allison, E. R. Bishop, and A. L. Sommer, *ibid.*, p. 616; *A.*, 353.

[4] V. V. Narliker, *Nature*, 1932, **129**, 402; *A.*, 442.

[5] *Ann. Reports*, 1930, **27**, 57.

[6] *Ibid.*, 1929, **26**, 44.

[7] *Ibid.*, 1929, **26**, 51; 1930, **27**, 62, 65; 1931, **28**, 55.

[8] *Ibid.*, 1929, **26**, 40.

IV. *Work on the Older Elements and their Compounds.*

This, of course, includes the great majority of the inorganic work published and can be sub-divided as follows :—

(i) *Study of the valency stages.* Numerous complex compounds of bivalent silver have now been prepared.[11] Several of the rare-earth metals form well-defined bivalent compounds, notably samarium, europium, and ytterbium,[12] which may be of great analytical significance since the bivalent metals can be separated with great readiness from those which remain tervalent. The bromides of ter- and bi-valent zirconium have been prepared [13] and compounds of univalent platinum and palladium.[14]

(ii) *Value of the co-ordination number and spatial character of the co-ordination and linkages.* It is important to know, not only the valencies of the elements in the old-fashioned sense, but also the co-ordination values, in Werner's sense, with which they can act. A certain amount of work now being done aims at determining these values.[15] The spatial arrangement of the co-ordinated atoms or groups provokes investigations in connexion with the problem of optical activity associated with special elements. Optically active 6-co-ordinated nickelous compounds were recently prepared.[16] It is, however, the problem of the 4-co-ordinated atom which arouses most interest. Although the configuration is usually tetrahedral, it can apparently be coplanar in special circumstances. Tellurium and platinum compounds of the type PtX_2Y_2 have received much attention in this connexion.[17]

Three important theoretical papers have been published on the nature of chemical linkages.[18] In the first paper several rules are formulated for electron-pair linkings, and the conditions specified under which four strong linkings in one plane directed towards the corners of a square become possible. In the second paper the conditions of stability of single- and triple-electron linkings are defined. The conditions for single linking are found in the boron hydrides and for triple linking in nitric oxide, nitrous oxide, and oxygen. The third paper deals with the transition from ionic to electron-pair linkages.

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[9] This vol., p. 77.

[10] *Ann. Reports*, 1930, **27**, 52.

[11] *Ibid.*, 1931, **28**, 51.

[12] *Ibid.*, 1929, **26**, 49; 1930, **27**, 63.

[13] *Ibid.*, 1931, **28**, 55.

[14] *Ibid.*, 1930, **27**, 76.

[15] *Ibid.*, 1930, **27**, 54; 1931, **28**, 51; this vol., p. 78.

[16] *Ibid.*, 1931, **28**, 61.

[17] *Ibid.*, 1929, **26**, 60, 80; 1930, **27**, 150, 164; 1931, **28**, 62; this vol., p. 92.

[18] L. Pauling, *J. Amer. Chem. Soc.*, 1931, **53**, 1367, 3225; **54**, 988; *A.*, 1931, 670, 1356; 1932, 561.

Much recent work[19] on the electrical conductivity, diffusivity, and reactivity at high temperatures of a number of spinels, silicates, germanates, molybdates, and tungstates in the solid condition appears to show that the structure of such compounds may be of two types. They may have an ionic lattice with conductivity of an ionic nature and a relatively high diffusivity, or a double oxide lattice in which the conductivity is electronic and the diffusivity much lower. It would seem that some kind of equilibrium between the two types of structure exists but that, at any rate in some cases, the double oxide type tends to become the more stable form at higher temperatures. Thus, Mg_2GeO_4 has a transformation point at 1065°. At lower temperatures it crystallises in a spinel type, and at higher temperatures it is isomorphous with olivine, Mg_2SiO_4. The spinel type has a higher electrical conductivity which is at least partly ionic, whilst the conductivity of the olivine type is electronic and associated with, mainly, a double oxide lattice. In the case of double halides there is, similarly, a transition between complex salt and aggregate of simple halides.

It is well known that salts, *e.g.*, cobalt sulphate, which, from the point of view of low-temperature reactions, are best considered in terms of $Co^{\bullet\bullet}$ and SO_4'' ions, behave at high temperatures in a fashion which is most conveniently interpreted on the old dualistic lines in terms of CoO and SO_3. The above results appear to have some bearing on this matter.

(iii) *Isolation of previously unknown simple compounds.* Many such compounds might be mentioned, but the oxides of fluorine and bromine are perhaps the most striking.[20]

(iv) *Phase-rule examination of various systems.* An immense amount of work is being done on these lines. Phase-rule methods are frequently the only ones by which the existence or non-existence of particular compounds can be decided with certainty. Much of this work relates to aqueous systems and has important bearings on many industrial processes. Various non-aqueous systems have of recent years been examined in connexion with slag equilibria in metallurgical processes. Much of metallurgy consists of the phase-rule examination of metal systems by special methods, among which *X*-ray examination plays an increasingly important part. References to practically all the systems examined in the last few years are given in the *Annual Reports.* A great deal of Inorganic Chemistry still requires revision by phase-rule methods.

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[19] W. Jander, *Z. angew. Chem.*, 1931, **44**, 870; *A.*, 1931, 1356; *Z. anorg. Chem.*, 1930, **192**, 286, 295; 1931, **199**, 306; *A.*, 1930, 1351; 1931, 1236; W. Jander and W. Stamm, *ibid.*, 1931, **199**, 165; 1932, **207**, 289; *A.*, 1931, 999; 1932, 985.

[20] *Ann. Reports*, 1929, **26**, 63; 1930, **27**, 71.

(v) *Miscellaneous.* Most of the remaining work can be grouped under the heads of new methods of preparation, preparation of new compounds of well-known types, study of the course or mechanism of reactions, but none calls for special mention here with the exception of oxidation,which has been the cause of much work on the corrosion and " passivity " of metals.[21]

Group 0.

The formation of compounds of krypton with chlorine and bromine has been announced.[22] It is clear that this requires confirmation and verification.

Liquid helium continues to be used for obtaining temperatures in the neighbourhood of the absolute zero. Carbides, nitrides, borides, and silicides of the heavier metals become superconductors at very low temperatures.[23] An interesting account and discussion of superconductivity has been given by J. C. McLennan and his co-workers.[24]

Group I.

A hydrogen isotope of mass two appears to be well established[25] and should be of great importance in the study of isotopes if the preliminary account of the enrichment of the residues of electrolytic hydrogen plants in this isotope should be confirmed by further work.[26] By the action of atomic hydrogen on oxygen at low temperatures there is formed what is considered to be a new form of hydrogen peroxide[27]—possibly with the structure $\substack{H\\H}\!>\!O\colon O$. At $-115°$ it changes into the ordinary form with partial decomposition; 97% of the theoretical yield of hydrogen peroxide is said to be obtained when hydrazobenzene in alcoholic solutions is converted into azobenzene by the action of gaseous oxygen.[28]

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[21] *Ann. Reports*, 1929, **26**, 38; 1930, **27**, 55.

[22] A. von Antropoff, K. Weil, and H. Frauenhof, *Naturwiss.*, 1932, **20**, 688; *A.*, 1007.

[23] W. Meissner, H. Franz, and H. Westerhoff, *Z. Physik*, 1932, **75**, 521; *A.*, 566.

[24] *Nature*, 1932, **130**, 879; *A.*, 1193.

[25] H. Kallmann and W. Lasarev, *Naturwiss.*, 1932, **20**, 472; *A.*, 790; N. S. Grace, *J. Amer. Chem. Soc.*, 1932, **54**, 2562; *A.*, 790.

[26] E. W. Washburn and H. C. Urey, *Proc. Nat. Acad. Sci.*, 1932, **18**, 496; H. C. Urey, F. G. Brickwedde, and G. M. Murphy, *Physical Rev.*, 1932, [ii], **40**, 1; *A.*, 554.

[27] K. H. Geib and P. Harteck, *Ber.*, 1932, **65**, [*B*], 1551; *A.*, 1098.

[28] J. H. Walton and G. W. Filson, *J. Amer. Chem. Soc.*, 1932, **54**, 3228; *A.*, 1098.

The vapour pressures of normal hydrogen (the mixture of ortho- and para-hydrogen which is in equilibrium at room temperature) and of para-hydrogen have been measured up to 1 atm. The normal b. p.'s have been determined as $-252{\cdot}754^\circ$ and $-252{\cdot}871^\circ$ respectively.[29]

Apparatus has been described for preparing and handling alkali-metal hydrides without exposure to air. All members of the series have the sodium chloride structure.[30] Excellent yields of lithium aryls and of butyl-lithium are obtainable under essentially the same conditions as those used for the related Grignard reagents.[31]

Lithium chloride monohydrate forms solid solutions with $2LiCl,CoCl_2,2H_2O$ ($= [Li_2(H_2O)_2]^{\cdot\cdot}[CoCl_4]''$).[32] From this fact it is concluded that the monohydrate is termolecular with the structure $\left[Li \begin{matrix} H_2O \\ H_2O \end{matrix} Li\right]^{\cdot\cdot} \left[Li \begin{matrix} Cl_3 \\ H_2O \end{matrix}\right]''$. The polymerisation is determined by the need for the lithium atom to become either 2- or 4-co-ordinated. The two lithium atoms in the complex kation are linked through the oxygen of the two water molecules.

In presence of moisture a 93% conversion of potassium chloride to nitrate can be obtained by the action of nitrogen peroxide. Nitrosyl chloride is formed at the same time.[33]

The polyhalogen compounds of the alkali metals continue to attract interest. No anhydrous perbromide of potassium exists, but $2KBr_6,3H_2O$ separates at 0° from concentrated solutions.[34] $CsBr_3$ can be obtained however.[34] $KIBr_2,H_2O$ [35] and $KI_9,3C_6H_6$[36] have been described; also $HI_3,4C_7H_5N$; $LiI_3,4C_7H_5N$; $KI_3,2C_7H_5N$.[37] Rubidium resembles cæsium in being able to form a solid polyiodide, RbI_3, whereas potassium cannot do so unless combined water, benzene, or other addenda are also present.[38] $RbFICl_3$ and $CsFICl_3$ have been prepared.[39]

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[29] W. H. Keesom, A. Bijl, and (Miss) H. van der Horst, *Proc. K. Akad. Wetensch. Amsterdam*, 1931, **34**, 1223; *A.*, 453.

[30] E. Zintl, A. Harder, and E. Husemann, *Z. physikal. Chem.*, 1931, [*B*], **14**, 265; *A.*, 1931, 1358.

[31] H. Gilman, E. A. Zoellner, and W. M. Selby, *J. Amer. Chem. Soc.*, 1932, **54**, 1957; *A.*, 728.

[32] H. Bassett and (Miss) I. Sanderson, *J.*, 1932, 1855; *A.*, 811.

[33] C. W. Whittaker, F. O. Lundstrom, and A. R. Merz, *Ind. Eng. Chem.*, 1931, **23**, 1410; *B.*, 304.

[34] I. W. H. Harris, *J.*, 1932, 1694, 2709; *A.*, 822.

[35] G. H. Cheesman and J. H. Martin, *ibid.*, p. 586; *A.*, 350.

[36] H. W. Foote and W. M. Bradley, *J. Physical Chem.*, 1932, **36**, 673; *A.*, 48.

[37] J. H. Martin, *J.*, 1932, 2640; *A.*, 1205.

[38] T. R. Briggs and E. S. Patterson, *ibid.*, p. 2621; *A.*, 1216.

[39] H. S. Booth, C. F. Swinehart, and W. C. Morris, *J. Amer. Chem. Soc.*, 1932, **54**, 2561; *A.*, 823; *J. Physical Chem.*, 1932, **36**, 2779; *A.*, 1219.

The dissociation pressures of silver oxide have been measured between 173° and 192°.[40] The solution of oxygen in molten silver and the phenomenon of spitting on solidification are due to formation of Ag_2O.[41]

Group II.

Beryllium of such purity that it dissolves in ordinary reagents only with difficulty can be obtained by electrolysis of solutions of the chloride or nitrate in liquid ammonia.[42] Many other metals can be successfully deposited from solutions in liquid ammonia.[43]

The fluoberyllates as a class appear to be isomorphous with the corresponding sulphates. Many of them have been prepared and examined.[44]

It is said that $Mg(SH)OH$, MgS_4, and MgS_5 can be stabilised in the form of compounds with two molecules of hexamethylenetetramine and ten of water.[45]

The calcium silicates and aluminates, owing to their importance in connexion with cement, continue to attract several workers.[46]

Pure anhydrous zinc chloride can be conveniently prepared in quantity by the action of dry hydrogen chloride on pure zinc in anhydrous ether.[47]

The true solubilities in mercury of the metals of atomic numbers 22—29 and of molybdenum, tungsten, and uranium have been determined by an improved method. These are in all cases very small even though, as in the case of copper, it may be possible to disperse considerable amounts of metal in the mercury.[48] A whole series of what may be called low-temperature alloys have been prepared and investigated by a novel and interesting method involving the use of solutions of metals in mercury.[49] These alloys are prepared either by admixture of the separate amalgams or by interaction of one amalgam with an aqueous solution of a salt of the other metal. The character of the compounds formed is deduced from their behaviour with acidified permanganate or other oxidising agents.

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[40] A. F. Benton and L. C. Drake, *J. Amer. Chem. Soc.*, 1932, **54**, 2186; *A.*, 810.

[41] J. H. Simons, *J. Physical Chem.*, 1932, **36**, 652; *A.*, 457; N. P. Allen, *Inst. Metals*, Sept. 1932, Advance Copy; *A.*, 1090.

[42] H. S. Booth and G. G. Torrey, *J. Physical Chem.*, 1931, **35**, 3111; *A.*, 129.

[43] H. S. Booth and M. Menahem, *ibid.*, p. 3303; *A.*, 129.

[44] N. N. Rây, *Z. anorg. Chem.*, 1931, **201**, 289; 1932, **205**, 257; **206**, 209; *A.*, 131, 582, 706.

[45] A. Tettamanzi, *Gazzetta*, 1932, **62**, 597; *A.*, 1098.

[46] H. Ehrenberg, *Z. physikal. Chem.*, 1931, [*B*], **14**, 421; *A.*, 131; E. T. Carlson, *Bur. Stand. J. Res.*, 1931, **7**, 893; *A.*, 131; S. Nagai, *J. Soc. Chem. Ind. Japan*, 1931, **34**, 418B; 1932, **35**, 182B, 320B, 380B, 394B; *A.*, 131, 707, 1008, 1217; *idem*, *Z. anorg. Chem.*, 1932, **206**, 177; **207**, 313; *A.*, 707, 1008.

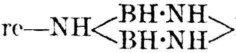
[47] R. T. Hamilton and J. A. V. Butler, *J.*, 1932, 2283; *A.*, 1008.

[48] N. M. Irvin and A. S. Russell, *ibid.*, p. 891; *A.*, 457.

[49] A. S. Russell, P. V. F. Cazalet, and N. M. Irvin, *ibid.*, pp. 841, 852; *A.*, 456; A. S. Russell and H. A. M. Lyons, *ibid.*, p. 857; *A.*, 456; A. S. Russell, T. R. Kennedy, J. Howitt, and H. A. M. Lyons, *ibid.*, p. 2340; *A.*, 1082.

The compounds obtained are in many cases entirely different from those found in alloys prepared by the usual high-temperature methods and this was to be expected. The compounds found in ordinary alloys were, however, also obtained. A very large number of new intermetallic compounds have been found by the new method, some of which contain mercury. Many of the compounds do not obviously belong to any class known to metallurgists but all of them follow the simple rule that their empirical formulæ correspond to total valency electrons equal to 6, 9, or 12 or some simple multiple of these numbers.

Group III.

Crystallised boron of metallic appearance and 99% purity is obtained by passing very condensed high-frequency sparks between electrodes of molybdenum or tungsten in a mixture of hydrogen and boron trichloride vapour.[50] New methods have been described for preparing B_2H_6, B_2H_5Br, and B_5H_9,[51] and reasons given for assigning $B_3N_3H_6$ a structure  $-\mathrm{NH}<\begin{matrix}\mathrm{BH{\cdot}NH}\\ \mathrm{BH{\cdot}NH}\end{matrix}>\mathrm{BH}-$ recalling that of benzene.[52] The compounds BBr_3,HCN and $BBr_3,AgCN$ have been prepared.[53]

A convenient method for preparing anhydrous aluminium bromide has been given.[54] Aluminium chloride forms a white compound $AlCl_3,2HCN$ with hydrogen cyanide.[55] Tensimetric and other measurements have been made on the numerous ammines of aluminium chloride, bromide, and iodide.[56] The mono-ammines in all cases are unimolecular non-ionic compounds $[AlX_3,NH_3]$. Alkali or alkaline-earth permutites become blue when treated with alkali sulphide or polysulphide solution in presence of air. In absence of air, only the polysulphides cause formation of the blue compound since the sulphide adsorption complex or compound is colourless. If the blue polysulphide permutites are prepared at temperatures above about 200° they are much more stable and yield the same X-ray diagram as ultramarine.[57] Base exchange by zeolites (permutites) can be applied so as to afford almost quantitative yields of salts by double decomposition even when the ordinary reaction between the solutions is incomplete.[58]

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[50] L. Hackspill, A. Stieber, and R. Hocart, *Compt. rend.*, 1931, **193**, 776; *A.*, 1931, 1377.

[51] H. I. Schlesinger and A. B. Burg, *J. Amer. Chem. Soc.*, 1931, **53**, 4321; *A.*, 350.

[52] A. Stock and R. Wierl, *Z. anorg. Chem.*, 1931, **203**, 228; *A.*, 215.

[53] E. Pohland, *ibid.*, **201**, 282; *A.*, 132.

[54] R. P. Bell, *J.*, 1932, 338; *A.*, 239.

[55] L. E. Hinkel and R. T. Dunn, *J.*, 1931, 3343; *A.*, 132.

[56] W. Klemm and E. Tanke, *Z. anorg. Chem.*, 1931, **200**, 343; *A.*, 1931, 1380; W. Klemm, E. Clausen, and H. Jacobi, *ibid.*, p. 367; *A.*, 1931, 1380.

A dark brown sublimate of Ga_2O is obtained by heating a mixture of the metal and the trioxide in a stream of hydrogen at 500—700°. GaO could not be prepared.[59]

$GaBr_3,6NH_3$ and $GaI_3,6NH_3$, stable at room temperature in absence of moisture, are formed by the action of liquid ammonia on the halides.[60] GaN, which sublimes without decomposition above 800°, can be prepared by the action of ammonia on gallium at 900—1000°.[61]

The alloys of lanthanum with Pb, Sn, Tl, Mg, Cu, Ag, and Au have been studied and several compounds were found in each case.[62] La, Ce, Nd, and Pr form compounds with mercury of the type M,Hg_4.[63]

Conductivity measurements on solutions of the normal and acid sulphates, and determinations of the degree of hydrolysis of the normal sulphates, have been utilised to determine the basicity of a number of the rare-earth metals.[64]

Measurements of the solubility products of the hydroxides under suitable conditions have been used for the same purpose [65] and, on the assumption that the solubility product is proportional to the basicity, the relative values of the latter for the metals Y, La, Pr, Nd, Sm, Gd, and Dy are found to be 1 : 1300 : 80 : 47 : 8 : 3·4 : 0·5. It is difficult to believe that there is so much difference between lanthanum and praseodymium.

A full account has been published of the preparation, properties, and reactions of ytterbium di- and tri-halides. Reduction of anhydrous tri-chloride or -bromide by hydrogen is the best method for preparing the dihalides, but the di-iodide can be prepared by dissociation of the tri-iodide in a vacuum at 600°.

The dichloride and dibromide on strong heating break up into metal and the trihalide. Aqueous solutions of the dihalides are yellowish and slowly evolve hydrogen—the more rapidly the greater the acidity. The iodide oxidises most slowly.[66]

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[57] E. Gruner and E. Hirsch, *Z. anorg. Chem.*, 1932, **204**, 232, 247; *A.*, 350.

[58] G. Austerweil, *Bull. Soc. chim.*, 1932, [iv], **51**, 729; *A.*, 1007.

[59] A. Brukl and G. Ortner, *Z. anorg. Chem.*, 1931, **203**, 23; *A.*, 238.

[60] W. C. Johnson and J. B. Parsons, *J. Amer. Chem. Soc.*, 1932, **54**, 2588; *A.*, 1218.

[61] W. C. Johnson, J. B. Parsons, and M. C. Crew, *ibid.*, p. 2651; *A.*, 1218.

[62] G. Canneri, *Met. Ital.*, 1931, **23**, 803; *Chem. Zentr.*, 1931, ii, 3035; *A.*, 455.

[63] P. T. Daniltschenko, *J. Gen. Chem. Russ.*, 1931, **1**, 467; *A.*, 1931, 1381.

[64] B. Brauner and E. Švagr, *Coll. Czech. Chem. Comm.*, 1932, **4**, 49, 239; *A.*, 470, 894.

[65] G. Enders, *Z. anorg. Chem.*, 1932, **205**, 321; *A.*, 696.

Anhydrous chlorides of the cerium group metals have been prepared from the anhydrous benzoates by the action of a saturated solution of hydrogen chloride in dry ether.[67]

Lanthana appears to form both a tri- and a mono-hydrate.[68]

Group IV.

Metallic sodium reacts smoothly with warm xylene solutions of phenyl or alkyl carbonates to yield pure dry carbon monoxide.[69] The preparation and properties of carbonyl sulphide and selenide [70] and of cyanogen fluoride [71] and oxycyanogen, $(OCN)_x$,[72] have been examined.

Support has been found for four of the five silicic acids described by earlier workers,[73] and conclusions have been drawn as to the p_H under which SiO_3'' and Si_2O_5'' ions can exist in solution.[74] Silica volatilises in supercritical steam (365—410°, 200—350 atm.) and then attacks various metallic oxides. A number of silicates have been synthesised in this way and the process appears to be of considerable mineralogical significance.[75] Several papers have been published on germanium dioxide, on the hydrated dioxide, and on the germanates.[76] The behaviour found recalls that of the silicon compounds.

Several salts of 10-tungstogermanic acid have been described.[77] A number of ammines of germanium iodide have been described,[78] but no evidence is given that they are definite compounds and that no reactions have occurred such as those between ammonia and germanium chloride.[79]

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[66] G. Jantsch, N. Skalla, and H. Jawurek, *Z. anorg. Chem.*, 1931, **201**, 207; *A.*, 30.

[67] P. Brauman and S. Takvorian, *Compt. rend.*, 1932, **194**, 1579; *A.*, 584.

[68] G. F. Hüttig and M. Kantor, *Z. anorg. Chem.*, 1931, **202**, 421; *A.*, 125.

[69] S. T. Bowden and T. John, *Nature*, 1932, **129**, 833; *A.*, 707.

[70] T. G. Pearson and P. L. Robinson, *J.*, 1932, 652; T. G. Pearson, P. L. Robinson, and J. Trotter, *ibid.*, p. 660; *A.*, 329.

[71] V. E. Cosslett, *Z. anorg. Chem.*, 1931, **201**, 75; *A.*, 31.

[72] H. Hunt, *J. Amer. Chem. Soc.*, 1932, **54**, 907; *A.*, 482.

[73] A. Simon and P. Rath, *Z. anorg. Chem.*, 1931, **202**, 191; *A.*, 122; *Ann. Reports*, 1929, **26**, 50; 1930, **27**, 64.

[74] G. Jander and W. Heukeshoven, *Z. anorg. Chem.*, 1931, **201**, 361; *A.*, 124.

[75] C. J. van Nieuwenburg and H. B. Blumendal, *Rec. trav. chim.*, 1931, **50**, 129, 989; *A.*, 322, 1381.

[76] A. W. Laubengayer and P. L. Brandt, *J. Amer. Chem. Soc.*, 1932, **54**, 549, 621; *A.*, 483; A. W. Laubengayer and D. S. Morton, *ibid.*, p. 2303; *A.*, 905; R. Schwarz and E. Huf, *Z. anorg. Chem.*, 1931, **203**, 188; *A.*, 117; R. Schwarz and F. Heinrich, *ibid.*, 1932, **205**, 43; *A.*, 584; R. Schwarz and G. Trageser, *ibid.*, **208**, 65; *A.*, 1099.

[77] A. Brukl and B. Hahn, *Monatsh.*, 1932, **59**, 194; *A.*, 351.

[78] T. Karantassis and L. Capatos, *Compt. rend.*, 1931, **193**, 1187; *A.*, 132.

The reactions and decompositions of stannous nitrate have been investigated,[80] and evidence obtained for a tri- and a mono-hydrate of stannic oxide.[81]

The action of ammonia on the tetrachlorides of tin and lead is very complex.[82] A number of compounds formed in the reaction with the former or by further treatment of the products have been isolated, such as $SnCl_4,2NH_3$, which appears to be a true ammine, the triamino-chloride $Sn(NH_2)_3Cl$, the nitrilo-chloride SnNCl, and the nitride Sn_3N_4. Lead also yields the nitrilo-chloride, PbNCl, and a very explosive compound derived from this by loss of lead chloride.

There is still difference of opinion as to whether lead suboxide really exists.[83] All the other oxides of lead have a definite crystal structure with the exception of the sesquioxide which is amorphous,[84] and there seems some doubt whether Pb_2O_3 represents a definite compound. The absorption and removal of oxygen in the reactions $PbO \rightleftharpoons Pb_3O_4 \rightleftharpoons PbO_2$ have been followed by means of oxygen-pressure measurements and *X*-ray examination of the crystal lattices.[85] With absorption of oxygen, the lattice of lead oxide or triplumbic tetroxide persists up to a definite oxygen content, whereupon red lead or the peroxide appears as a second phase. Similarly on removal of oxygen the lattice of PbO_2 or Pb_3O_4 persists over a certain range without any indications of Pb_2O_3 or Pb_3O_5. There does, however, appear to be a second, black, modification of triplumbic tetroxide.

Several intermediate stages have been detected in the decomposition of lead nitrate in molten potassium nitrate.[86]

All the alkali-metal fluotitanates have been prepared and described, and their reactions and solubilities determined.[87] A number of complex iodates of titanium have also been described.[88]

Black crystals of Th_3N_4 were prepared by electrically heating to

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[79] *Ann. Reports*, 1930, **27**, 65.

[80] C. Montemartini and E. Vernazza, *Ind. chim.*, 1931, **6**, 632; *A.*, 351.

[81] A. Simon and P. Rath, *Z. anorg. Chem.*, 1931, **202**, 200; *A.*, 122.

[82] R. Schwarz and A. Jeanmaire, *Ber.*, 1932, **65**, [*B*], 1443; *A.*, 1100.

[83] P. Pascal and P. Minne, *Compt. rend.*, 1931, **193**, 1303; *A.*, 132; M. Le Blanc and E. Eberius, *Z. physikal. Chem.*, 1932, **160**, 129; *A.*, 823; R. Fricke and P. Ackermann, *ibid.*, **161**, 227; *A.*, 1100.

[84] J. A. Darbyshire, *J.*, 1932, 211; *A.*, 326.

[85] M. Le Blanc and E. Eberius, *Z. physikal. Chem.*, 1932, **160**, 69; *A.*, 697.

[86] K. Laybourn and W. M. Madgin, *J.*, 1932, 1360; *A.*, 707.

[87] H. Ginsberg and G. Holder, *Z. anorg. Chem.*, 1931, **201**, 193; *A.*, 31; H. Ginsberg, *ibid.*, 1932, **204**, 225; *A.*, 351.

[88] P. R. Rây and H. Saha, *ibid.*, **208**, 100; *A.*, 1099.

2220—2600° a compressed mixture of thoria, graphite, and tungsten in a non-oxidising atmosphere containing nitrogen.[89]

Group V.

The nitric oxide liberated at the anode in the early stages of the electrolysis of fused sodium nitrite results from the secondary reaction $NaNO_2 + NO_2 \rightleftarrows NaNO_3 + NO$, but although nitrite was completely oxidised to nitrate in 3—4 hours in a current of nitrogen peroxide at 315—450°, only about 5% of nitrate was reduced by nitric oxide in 6—7 hours at 315°.[90] Nitric oxide is absorbed by alkaline sulphite solutions to yield compounds which react like M_2SO_4,N_2O since they decompose slowly in cold, and rapidly in hot, water to yield sulphate and nitrous oxide. Very pure nitrous oxide can be obtained by the action of dilute sulphuric acid on solutions of K_2SO_4,N_2O, the gas being washed with 4*N*-potassium hydroxide and water. By addition of K_2SO_4,N_2O to solutions of suitable manganese, cobalt, zinc, or cadmium salts, complex salts were formed of the type $K_4M(SO_4,N_2O)_3,2H_2O$ or, in the case of cadmium, $K_2M(SO_4,N_2O)_2,2H_2O$.[91]

Phosphorous acid alone is formed when phosphorous oxide is shaken vigorously with excess of cold water. If there is no shaking, local overheating of the acid leads to formation of phosphine, while interaction between the acid and the oxide yields phosphoric acid and yellow, so-called, phosphorus suboxide.[92]

Both in neutral and in acid solutions, sodium metaphosphate combines with water to give orthophosphate only. $(NaPO_3)_6$ in neutral solution also gives rise only to orthophosphate, but in acid solution pyrophosphate also is formed.[93] A method for preparing the well-crystallised hexametaphosphate $Na_6(PO_3)_6,10H_2O$ has been given.[94] The equilibrium $H_3PO_4 + HF \rightleftarrows H_2PO_3F + H_2O$ has been studied at 20°. H_2PO_3F is also formed by the action of hydrogen fluoride on potassium dihydrogen phosphate and on sodium pyrophosphate, but potassium fluoride and potassium dihydrogen phosphate do not react either in dilute or in concentrated solution.[95]

NH_4PF_6 and KPF_6 can be obtained in good yield by the action of phosphorus pentachloride on ammonium or potassium fluoride.

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[89] W. Düsing and M. Hüniger, *Tech. wiss. Abh. Osram-Konz.*, 1931, **2**, 357; *Chem. Zentr.*, 1932, i, 203; *A.*, 584.

[90] J. Szper and K. Fiszman, *Z. anorg. Chem.*, 1932, **206**, 257; *A.*, 823.

[91] H. Gehlen, *Ber.*, 1931, **64**, [*B*], 1267; 1932, **65**, [*B*], 1130; *A.*, 922, 919.

[92] L. Wolf, W. Jung, and M. Tschudnowsky, *Ber.*, 1932, **65**, [*B*], 488; *A.*, 483.

[93] S. S. Dragunov and A. N. Rossnovskaja, *Z. anorg. Chem.*, 1931, **200**, 321; *A.*, 1931, 1372.

[94] P. Pascal and (Mme.) Réchid, *Compt. rend.*, 1932, **194**, 762; *A.*, 483.

[95] W. Lange and G. Stein, *Ber.*, 1931, **64**, [*B*], 2772; *A.*, 132.

With sodium fluoride reaction is much slower so that only a 5—6% yield of $NaPF_6$ is obtainable. Ammonium chloride and phosphorus pentachloride yield $(PNCl_2)_x$.[96]

The mechanism of the thermal conversion of arsenite into arsenate is invariably based on the reaction $5As_2O_3 \longrightarrow 3As_2O_5 + 4As$ and does not involve direct oxidation by atmospheric oxygen. In air arsenious oxide is formed, subsequently, from the arsenic liberated and then undergoes further decomposition.[97] Salt-like polyantimonides or polybismuthides Na_3Sb_7,xNH_3 (Na_3Bi_5,xNH_3) are formed by extracting sodium–antimony or –bismuth alloys with liquid ammonia.[98] When ammonia is removed, the complex anions break up and a mixture of metallic phases, Sb with NaSb or Bi with NaBi, results.

Antimony trichloride gives no ammine with ammonia. The substance regarded as $SbCl_3,3NH_3$ is really a mixture of ammonium chloride and, probably, Sb(NH)Cl. The latter yields SbN on extraction with liquid ammonia to remove the ammonium chloride.[99]

In the equilibrium $2Bi_2O_3 + Bi_2S_3 \rightleftharpoons 6Bi + 3SO_2$, evolution of sulphur dioxide begins at 150—200° and reaches a pressure of 1 atm. at 519°. Absorption of sulphur dioxide in the reverse reaction is measurable at 400°.[1]

A number of internally complex organic derivatives of tervalent vanadium have been prepared and compared with those of the corresponding iron compounds.[2] Conductometric and potentiometric titrations of solutions of potassium niobate with caustic alkali or hydrochloric acid gave no indications of the existence of ortho- or pyro-niobates but only of meta-compounds.[3]

Group VI.

A nearly quantitative yield of fluorosulphonic acid is obtained by distilling a mixture of oleum with potassium hydrogen fluoride. The dry acid does not attack glass.[4]

The m. p.'s, b. p.'s, densities, and surface tensions of selenium and tellurium hydrides have been recorded.[5]

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[96] W. Lange and G. von Krueger, *Ber.*, 1932, **65**, [*B*], 1253; *A.*, 1100.

[97] G. G. Reissans, *Z. angew. Chem.*, 1931, **44**, 959; *A.*, 130; E. R. Rushton, *J. Physical Chem.*, 1932, **36**, 1772; *A.*, 810.

[98] E. Zintl and W. Dullenkopf, *Z. physikal. Chem.*, 1932, [*B*], **16**, 183; *A.*, 455; *Ann. Reports*, 1929, **26**, 42.

[99] R. Schwarz and A. Jeanmaire, *Ber.*, 1932, **65**, [*B*], 1662.

[1] R. Schenck and F. Speckmann, *Z. anorg. Chem.*, 1932, **206**, 378; *A.*, 810.

[2] A. Rosenheim, E. Hilzheimer, and J. Wolff, *ibid.*, 1931, **201**, 162; *A.*, 31.

[3] H. T. S. Britton and R. A. Robinson, *J.*, 1932, 2265; *A.*, 999.

[4] J. Meyer and G. Schramm, *Z. anorg. Chem.*, 1932, **206**, 24; *A.*, 708.

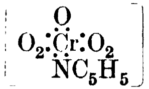
[5] P. L. Robinson and W. E. Scott, *J.*, 1932, 972; *A.*, 454.

Selenium dioxide has been found to be a useful oxidising agent for the preparation of a number of organic compounds.[6] Solubilities of the normal and acid selenites of sodium and potassium have been determined and the composition of the salts and their hydrates established.[7]

Pure chromous iodide has been prepared by heating electrolytic chromium with an excess of iodine in nitrogen or vacuum at 1150—1200° and removing excess of iodine from the product by heating at 200°.[8]

The specific action of chromates in inhibiting corrosion of iron is due to the fact that CrO_4'' ion precipitates $Fe^{\cdot\cdot}$ ion completely; the precipitate consists of the hydrated sesquioxides and has considerable protective action owing to its gelatinous nature, high specific volume, close adhesion to the iron, etc. Similar protective films form on chromium steels.[9]

The blue "perchromic acid" has hitherto been regarded as a true peroxidic acid $H{\cdot}O{\cdot}O{\cdot}CrO_3$, of which the pyridine and ammonia compounds were true salts. It was, however, difficult to understand how chromium could have the valency of 7 which is required by such a structure. Strong evidence has now been brought forward for believing that the blue compound is not an acid at all but a non-ionic co-ordination complex of the peroxide CrO_5, $O{=}Cr{\lessdot}^{O_2}_{O_2}$, with pyridine, ether, etc., in which the chromium still has a valency of six, with co-ordination number 4. The pyridine compound, on this basis, becomes



$$\left[\begin{matrix} & O & \\ O_2 & \overset{\cdot\cdot}{\underset{\cdot\cdot}{:Cr:}} & O_2 \\ & NC_5H_5 & \end{matrix}\right]$$

.[10]

Molybdenum sesquisulphide must be prepared by heating the disulphide under ordinary pressure, not in a vacuum.[11] The complex cyanide of tervalent molybdenum $K_4Mo(CN)_7,2H_2O$ [12] and the red permolybdates K_2MoO_8 and $Zn(NH_3)_4MoO_8$ have been prepared,[13] while the preparation and reactions of the red $K_4[Mo(CN)_4(OH)_4]$ have been discussed.[14] Methods have been given for preparing several sodium salts of phosphomolybdic and phosphotungstic acids.[15] $WOCl_4$ is best prepared by passing chlorine over an equimolecular mixture of tungsten and its dioxide at 700—800°. It is purified by distillation in vacuum or in a stream of carbon dioxide at 200°. Careful measurements of a number of its physical constants have been made.[16] Some reactions of tungsten hexachloride have been described.[17]

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[6] H. L. Riley, J. F. Morley, and N. A. C. Friend, *J.*, 1932, 1875; *A.*, 833; H. L. Riley and N. A. C. Friend, *ibid.*, p. 2342; *A.*, 1108.

[7] J. Janitzki, *Z. anorg. Chem.*, 1932, **205**, 49; *A.*, 584.

[8] F. Hein and I. Wintner-Hölder, *ibid.*, 1931, **202**, 81; *A.*, 133.

[9] T. P. Hoar and U. R. Evans, *J.*, 1932, 2476; *A.*, 1093.

[10] R. Schwarz and H. Giese, *Ber.*, 1932, **65**, [*B*], 871; *A.*, 708; E. H. Riesenfeld, *ibid.*, p. 1868.

[11] Guichard, *Bull. Soc. chim.*, 1932, [iv], **51**, 563; *A.*, 708.

[12] R. C. Young, *J. Amer. Chem. Soc.*, 1932, **54**, 1402; *A.*, 584.

[13] K. Gleu, *Z. anorg. Chem.*, 1932, **204**, 67; *A.*, 484.

[14] W. F. Jakób and E. Turkiewicz, *Rocz. Chem.*, 1931, **11**, 569; *A.*, 1931, 1382; W. F. Jakób and C. Michalewicz, *ibid.*, 1932, **12**, 567; *A.*, 1100.

Mixtures of WC and W_2C are formed when the elements are heated together at temperatures between 1600° and 2500°. The former can be separated from the reaction products by heating in chlorine below 600° since the metal and the other carbide are converted into volatile chlorides while WC remains unaffected.[18]

A number of complex salts and ammines of quadri- and sexavalent uranium have been described, as well as a number of peruranates.[19]

Group VII.

Various physical properties of boron and bromine trifluorides and arsenic pentafluoride have been measured.[20] A number of complex fluorides of tervalent vanadium and chromium of the types $M_3[V(\text{or } Cr)F_6]$ and $M_2[V(\text{or } Cr)F_5,H_2O]$ have been prepared.[21] They all form cubic crystals.

Bromine pentafluoride has been obtained by heating the trifluoride with fluorine at 200°. It is a colourless fuming liquid, b. p. 40·5°. Its physical properties and reactions have been examined.[22]

Preliminary details have been given for preparing hypofluorous and fluoric acids.[23] Chlorine and bromine form the hydrates $Cl_2,6H_2O$ and $Br_2,10H_2O$, and $BrCl,4H_2O$ is more stable than either of these.[24] It is considered that there is little if any $I^{\bullet}$ ion in aqueous iodine monochloride, but that in hydrochloric acid solution there is considerable formation of ICl_2' ion.[25] It has been stated [26] that iodine dissociates in ethyl-alcoholic solution to yield uni- and tervalent ions. The former are precipitated by alcoholic silver nitrate, leaving $I(NO_3)_3$ in solution, and this, with excess of iodine, yields INO_3. Pyridine and quinoline compounds of these nitrates are described.

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[15] A. V. Rakovski and E. A. Nikitina, *J. Gen. Chem. Russ.*, 1931, **1**, 240, 247; *A.*, 1931, 1382.

[16] W. Reinders and J. A. M. van Liempt, *Rec. trav. chim.*, 1931, **50**, 997; *A.*, 1931, 1382.

[17] A. J. Cooper and W. Wardlaw, *J.*, 1932, 635; *A.*, 352.

[18] I. Iitaka and Y. Aoki, *Bull. Chem. Soc. Japan*, 1932, **6**, 108; *A.*, 708.

[19] R. Răşcanu, *Ann. sci. Univ. Jassy*, 1930, **16**, 32, 459; *A.*, 1931, 1382; A. Rosenheim and M. Kelmy, *Z. anorg. Chem.*, 1932, **206**, 31; *A.*, 708; A. Rosenheim and H. Daehr, *ibid.*, **208**, 81; *A.*, 1100.

[20] O. Ruff, A. Braida, O. Bretschneider, W. Menzel, and H. Plaut, *ibid.*, **206**, 59; *A.*, 707.

[21] L. Passerini and R. Pirani, *Gazzetta*, 1932, **62**, 279, 289; *A.*, 795; R. Pirani, *ibid.*, p. 380; *A.*, 902.

[22] O. Ruff and W. Menzel, *Z. anorg. Chem.*, 1931, **202**, 49; *A.*, 133.

[23] L. M. Dennis and E. G. Rochow, *J. Amer. Chem. Soc.*, 1932, **54**, 832; *A.*, 485.

[24] S. Anwar-Ullah, *J.*, 1932, 1172, 1176; *A.*, 585; I. W. H. Harris, *ibid.*, pp. 582, 2709; *A.*, 352.

The isobaric dissociation curve of manganese oxide at about 10 mm. shows the successive formation of Mn_2O_3, Mn_3O_4, and MnO; Mn_2O_7 appears to give the dioxide directly without any intermediate stage.[27] Several manganic dithiocarbamates have been prepared which are very similar to the corresponding ferric compounds.[28]

Evidence is given for the view that Re_2O_7 is the highest oxide of rhenium stable under ordinary conditions.[29] Further work has been published on the oxides and other compounds of ter-,[30] quadri-,[30] quinque-,[31] sexa-,[32] and septa- [33] valent rhenium, but much of this is in the nature of confirmation of earlier work. Some thermochemical measurements have been made on a few of the septavalent compounds.[34]

Group VIII.

The study of the corrosion of iron and other metals has been placed on a much more quantitative basis by measuring the absorption of oxygen and evolution of hydrogen which occur during the process. Important results have already been obtained in this way. Thus, it is found that when iron or steel corrodes in potassium chloride solutions the proportion of metal which corrodes owing to liberation of hydrogen is considerable for solutions more concentrated than 0·001*N*.[35]

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[25] J. H. Faull, jun., and S. Baeckström, *J. Amer. Chem. Soc.*, 1932, **54**, 620; *A.*, 467; *Ann. Reports*, 1930, **27**, 72.

[26] M. I. Uschakov, *J. Gen. Chem. Russ.*, 1931, **1**, 1258; *A.*, 809.

[27] A. Simon and F. Fehér, *Z. Elektrochem.*, 1932, **38**, 137; *A.*, 468. See also F. Krüll, *Z. anorg. Chem.*, 1932, **208**, 134; *A.*, 1204.

[28] L. Cambi and A. Cagnasso, *Atti R. Accad. Lincei*, 1931, [vi], **14**, 71; *A.*, 133.

[29] H. V. A. Briscoe, P. L. Robinson, and A. J. Rudge, *Nature*, 1932, **129**, 618; *A.*, 585.

[30] F. Krauss and H. Steinfeld, *Ber.*, 1931, **64**, [*B*], 2552; *A.*, 1931, 1382; W. Manchot, H. Schmid, and J. Düsing, *ibid.*, p. 2905; *A.*, 133; F. Krauss and H. Dählmann, *ibid.*, 1932, **65**, [*B*], 877; *A.*, 711; H. V. A. Briscoe, P. L. Robinson, and A. J. Rudge, *J.*, 1931, 3218; *A.*, 133; E. Turkiewicz, *Rocz. Chem.*, 1932, **12**, 589; *A.*, 1101.

[31] W. A. Roth and G. Becker, *Ber.*, 1932, **65**, [*B*], 373; *A.*, 353.

[32] W. Biltz, G. A. Lehrer, and K. Meisel, *Nach. Ges. Wiss. Göttingen*, 1931, 191; *Chem. Zentr.*, 1932, i, 1070; *A.*, 708; *idem*, *Z. anorg. Chem.*, 1932, **207**, 113; *A.*, 1008.

[33] H. V. A. Briscoe, P. L. Robinson, and A. J. Rudge, *J.*, 1932, 1104; *A.*, 585; A. Brukl and K. Ziegler, *Ber.*, 1932, **65**, [*B*], 916; *A.*, 708; W. Biltz and F. Weibke, *Z. anorg. Chem.*, 1931, **203**, 3; *A.*, 239.

[34] W. A. Roth and G. Becker, *Z. physikal. Chem.*, 1932, **159**, 27; *A.*, 469.

By the interaction of ferric chloride with alkali-metal thiocyanates in alcoholic solution, complex *ferrous* thiocyanates only are obtained, of the type $R_4[Fe(CNS)_6],xH_2O$. In aqueous solution ferric compounds are obtained and a large number of complex ferric thiocyanates have been described. The compound

$$C_5H_6N[Fe(C_5H_5N)_2(CNS)_4]$$

by boiling with pyridine is reduced to $[Fe(C_5H_5N)_4(CNS)_2]$, which, on atmospheric oxidation in chloroform solution, yields $[Fe_3(C_5H_5N)_{10}(CNS)_8]$ corresponding with Fe_3O_4.[36] The two ferric dithiocarbamates $[Me_2N·CS_2]_3Fe$ and $[C_5H_{10}N·CS_2]_3Fe$ have been prepared. These are stable towards oxygen and nitric oxide, but the corresponding ferrous compounds each combine with one molecule of this gas.[37] Under the influence of sodium ethoxide, iron pentacarbonyl reacts to form ethyl carbonate and $Fe(CO)_4Na_2$.[38] The latter gives the ether-soluble $Fe(CO)_4H_2$ with acid, and this, with concentrated mineral acid, decomposes into tetracarbonyl and hydrogen. It is pointed out that the production of $Fe(CO)_4H_2$ and carbon dioxide from the pentacarbonyl may be regarded as a form of hydrolytic water-gas reaction taking place at room temperature.

The reactions of iron pentacarbonyl with alkali or with organic bases seem to be often very complex, and a number of papers in addition to the one just cited deal with the matter.[39]

Several iron carbonyl halogen compounds have been prepared, derived by substitution either from $Fe(CO)_4X_2$ ($X = Cl$, Br, or I), *e.g.*, $(EtS·[CH_2]_2·SEt)Fe(CO)_2I_2$, or from $[Fe(CO)_4]_3$, *e.g.*, $[Fe(CO)_3Br_2]_3$.[40]

Carbon monoxide is lost by $[Co(CO)_4]_2$ at 55—60°, with formation of $[Co(CO)_3]_4$. The cobalt carbonyls show a great tendency towards polymerisation and high chemical reactivity. Nickel tetracarbonyl is considerably more stable than the iron or cobalt carbonyls. A number of derivatives of the cobalt and nickel compounds have been prepared.[41]

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[35] G. D. Bengough, J. M. Stuart, and A. R. Lee, *Proc. Roy. Soc.*, 1930, [*A*], **127**, 42; *A.*, 1930, 712; G. D. Bengough, A. R. Lee, and F. Wormwell, *ibid.*, 1931, [*A*], **134**, 308; *A.*, 27.

[36] A. Rosenheim, E. Roehrich, and L. Trewendt, *Z. anorg. Chem.*, 1932, **207**, 97; *A.*, 1009.

[37] L. Cambi, A. Cagnasso, and A. Tanara, *Atti R. Accad. Lincei*, 1931, [vi], **13**, 254; *A.*, 1931, 1382.

[38] H. Hock and H. Stuhlmann, *Chem.-Ztg.*, 1931, **55**, 874; *A.*, 32.

[39] F. Feigl and P. Krumholz, *Monatsh.*, 1932, **59**, 314; *A.*, 485; W. Hieber and F. Leutert, *Ber.*, 1931, **64**, [*B*], 2832; *A.*, 134; W. Hieber, F. Leutert, and (Frl.) E. Schmidt, *Z. anorg. Chem.*, 1932, **204**, 145; W. Hieber, H. Vetter, and H. Kaufmann, *ibid.*, p. 165; *A.*, 485; W. Hieber and F. Mühlbauer, *Ber.*, 1932, **65**, [*B*], 1082; *A.*, 920.

[40] W. Hieber, G. Bader, K. Ries, and E. Becker, *Z. anorg. Chem.*, 1931, **201**, 329; *A.*, 134.

A critical review of recent work on the equilibrium of systems involved in the production of steel has been published.[42] The systems Fe–O, Fe–FeO–CaO, Fe–O–C, Fe–Si–O, Fe–MnO, and others involving phosphorus and sulphur are considered, and a tabulated summary is given of the equilibrium constants obtained by the various workers.

The equilibria concerned in the cementation of iron have been the subject of a careful study. It is concluded from the results that carbon vapour is monatomic and that the distribution of free carbon between the vapour and the solid phase follows Henry's law.[43] The equilibria between ferrous oxide and silica have been examined in electrolytic iron crucibles in a vacuum and in pure nitrogen at temperatures below 1523°. The very interesting fact emerged that all melts in equilibrium with iron contain some ferric oxide, the percentage weight of which decreases rapidly from 11·5 as silica is added. This is presumably owing to an equilibrium $3FeO \rightleftharpoons Fe + Fe_2O_3$ of the well-known type to which lower valency stages are subject. On account of this, synthetic and natural fayalite (Fe_2SiO_4) and all $FeO–SiO_2$ mixtures melt incongruently, with separation of iron. The bearing of the results obtained on petrology and the problems of slag formation and furnace linings is discussed.[44]

The distribution of manganese between molten iron and slag owing to the equilibrium $FeO + Mn \rightleftharpoons Fe + MnO$ has been examined, and also the influence of additions of silica and lime.[45] Two calcium ferrites exist, CaO,Fe_2O_3 and $2CaO,Fe_2O_3$; they can be formed from calcium carbonate and ferric oxide at temperatures above 500°. $2CaO,Fe_2O_3$ does not decompose below 1400°, though ferric oxide evolves oxygen at 1380°. Lime also forms a compound with ferrous oxide which is probably $2CaO,FeO$.[46]

Mixtures of metal and several phosphides are obtained by the action of hypophosphite on solutions of cobalt or nickel salts.[47] Crystalline NiP is obtained by the interaction of phosphorus vapour and nickel tetracarbonyl at 50°. An amorphous black solid, probably NiP_4, is obtained by bubbling the carbonyl vapour through phosphorus, either liquid or dissolved in turpentine.[48]

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[41] F. Reiff, *Z. anorg. Chem.*, 1931, **202**, 375; *A.*, 239; W. Hieber and H. Kaufmann, *ibid.*, 1932, **204**, 174; *A.*, 485; W. Hieber, F. Mühlbauer, and E. A. Ehmann, *Ber.*, 1932, **65**, [*B*], 1090; *A.*, 920.

[42] F. Sauerwald and W. Hummitzsch, *Arch. Eisenhüttenw.*, 1931—1932, **5**, 355; *A.*, 340.

[43] A. Bramley and H. D. Lord, *J.*, 1932, 1641; *A.*, 811.

[44] N. L. Bowen and J. F. Schairer, *Amer. J. Sci.*, 1932, [v], **24**, 177; *A.*, 997.

[45] W. Krings and H. Schackmann, *Z. anorg. Chem.*, 1931, **202**, 99; 1932, **206**, 337; *A.*, 125, 811; E. Maurer and W. Bischof, *Iron and Steel Inst.*, May 1932, Advance Copy; *B.*, 602.

[46] J. Konarzewski, *Rocz. Chem.*, 1931, **11**, 516, 607; *A.*, 1931, 1010, 1373.

Several new cobaltic ammines have been described,[49] and a very large number of ruthenium compounds.[50]

Rhodium dioxide cannot be obtained anhydrous, but in hydrated form it may be obtained pure by the electrolysis of a solution prepared from Na_3RhCl_6 and potassium hydroxide. Dark green hydrated RhO_2 separates at the anode, but attempts to dehydrate it always result in the formation of Rh_2O_3.[51] At 210° $[BrRh(NH_3)_5]Br_2$ is quantitatively converted into $[Br_3Rh(NH_3)_3]$. The corresponding chlorine and iodine compounds do not behave in this way.[52] An inorganic compound containing no carbon but showing optical activity has at last been found in sodium diaquo-rhodium disulphamide, $Na[(H_2O)_2Rh(NH{\cdot}SO_2{\cdot}NH)_2]$, the *cis*-form of which has been resolved into a *d*- and an *l*-form.[53]

Nickel, ruthenium, rhodium, and palladium can apparently be reduced to the univalent state when suitable cyanide solutions are warmed with alkali and 90% sodium hypophosphite solution.[54] Palladous chloride with many purines and alkaloids forms almost insoluble compounds from which the bases are easily regenerated. The caffeine and theobromine complexes have the formula R_2PdCl_2.[55]

Much work published during the past year has centred round the question whether the valencies of 4-covalent compounds of the metals of Group VIII are planar or directed towards the corners of a tetrahedron. The conditions under which a planar configuration is possible have been deduced and can occur with bivalent nickel, palladium, and platinum.[56] A case of the kind appears to occur with the glyoximes of nickel, since the benzylmethylglyoxime has been obtained in two isomeric forms of the same molecular weight which are interpreted as *cis*- and *trans*-forms.[57]

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[47] R. Scholder and H. L. Haken, *Ber.*, 1931, **64**, [*B*], 2870; *A.*, 134.

[48] C. M. W. Grieb and R. H. Jones, *J.*, 1932, 2543.

[49] H. J. S. King, *J.*, 1932, 1275; *A.*, 585; T. Das-Gupta and P. B. Sarkar, *J. Indian Chem. Soc.*, 1932, **9**, 79; *A.*, 709.

[50] R. Charonnat, *Ann. Chim.*, 1931, [x], **16**, 123; *A.*, 1931, 1383.

[51] L. Wöhler and K. F. A. Ewald, *Z. anorg. Chem.*, 1931, **201**, 145; *A.*, 32.

[52] E. Birk and H. Kamm, Siebert Festschr., 1931, 12; *A.*, 240.

[53] F. G. Mann, *Nature*, 1932, **130**, 368; *A.*, 1101.

[54] W. Manchot and H. Schmid, *Ber.*, 1931, **64**, [*B*], 2672; *A.*, 32.

[55] J. M. Gulland and T. F. Macrae, *J.*, 1932, 2231; *A.*, 1052.

[56] L. Pauling, *J. Amer. Chem. Soc.*, 1931, **53**, 1367; *A.*, 1931, 670.

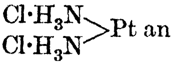
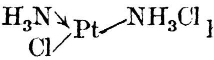
[57] S. Sugden, *J.*, 1932, 246; *A.*, 272.

Investigation [58] of the supposed *cis-* and *trans*-isomerides of PdA_2X_2 (where A is an amine and X an acid radical) appears to show, however, that in these cases such isomerism does not occur. The pink compounds are considered to have the formula $[PdA_4]PdX_4$, while the yellow compounds are $[PdA_2X_2]$. Other workers [59] agree that there is no *cis-trans*-isomerism in the case of $Pd(NH_3)_2Cl_2$ but consider that both the yellow and the pink form are bimolar.

From an *X*-ray examination of $[Pt(NH_3)_4]Cl_2,H_2O$ it is deduced that the four ammonia molecules have a planar configuration round the platinum atom. The water molecule is regarded as being at the cell centre and not midway between two platinum atoms as part of a six-point system round the platinum.[60] The solid solution formation said to occur [61] between $[Pt(NH_3)_4]Cl_2,H_2O$ and

$$4\{Pt(NH_3)_4Cl_2\}Pt(NH_3)_2Cl_2$$

was not confirmed. *X*-Ray investigations of the green salt of Magnus $[Pt(NH_3)_4][PtCl_4]$ show that the two complex ions have the same structures as those present in $[Pt(NH_3)_4]Cl_2,H_2O$ and in K_2PtCl_4; both are therefore considered to be planar. The corresponding pink salt of Magnus was shown to be very unstable and its precise nature is still uncertain.[62]

The problem of the isomeric diamminoplatinous chlorides has been complicated by the discovery of a third isomeride.[63] All three forms are considered to be, probably, structural isomerides and to be unimolecular and non-ionic. Only one form is supposed to have four groups arranged round the platinum atom, with no evidence available at present to show whether the arrangement is tetrahedral or planar. For the other two isomerides the early types of structures  $\begin{matrix}Cl\cdot H_3N\\ Cl\cdot H_3N\end{matrix}{>}Pt$ and  $\begin{matrix}H_3N\\ Cl\end{matrix}{>}Pt{-}NH_3Cl$ have been revived. The evidence advanced for this is lengthy, but to the reviewer it seems a retrograde step. In the groups $\cdot NH_3Cl$ the chlorine is considered to be attached to nitrogen which is 5-covalent with a decet of electrons. It is difficult to believe that such a structure would have the stability necessary to account for the behaviour of the compounds, and weightier evidence seems called for before discarding Sidgwick's covalency rule for nitrogen. It seems more likely that the three isomerides are not all monomeric.

In order to account for the remarkable isomerism found amongst the mixed tetrammino-dihalides, *e.g.*, $[Pt(NH_3)_2py_2]Cl_2$, it has been suggested [64] that the four linkings to the ammino-groups of the tetrammines are differentiated into two equivalent pairs which function independently, a closer relationship existing between the members of a pair than exists between either member of one pair and either member of the other. All four linkings are, however, supposed to be of the same kind, and precisely equivalent to one another in the sense of the equivalence of the six linkings to hydrogen in the benzene ring. Time alone can show whether such a view will be found satisfactory, but it has been found useful in interpreting the formation and reactions of a number of compounds.[58, 65]

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[58] H. D. K. Drew, F. W. Pinkard, G. H. Preston, and W. Wardlaw, *J.*, 1932, 1895; *A.*, 824.

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[60] E. G. Cox, *J.*, 1932, 1912; *A.*, 797.

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[63] H. D. K. Drew, F. W. Pinkard, W. Wardlaw, and E. G. Cox, *ibid.*, p. 988; *A.*, 562.

The view appears to be gaining ground that in 4-covalent platinum the groups may be grouped tetrahedrally about the platinum atom in some cases and be planar in others. To investigate this point still further, the two isomeric diquinolinoplatinous chlorides have been prepared for the first time in a pure condition.[66]

Systems and Equilibria.

Ag–Cu–Mn [67]; potassium phthalate–phthalic acid–water [68]; $Fe–O_2$ [69]; $CO–N_2–H_2$ and the component binary systems [70]; $Pr_2(SO_4)_3–Tl_2SO_4–H_2O$ [71]; $Pr_2(SO_4)_3–Na_2SO_4–H_2O$ [72]; $Li_2SO_4–Bi_2(SO_4)_3–H_2O$ [73]; $Na_2\{K_2,Rb_2,(NH_4)_2,Tl_2\}SO_4–Mg(Co,Ni,Zn,Cd)SO_4–H_2O$ [74]; $K_2(Rb_2,Tl_2)SO_4–CdSO_4–H_2O$ [75]; $CaO–Al_2O_3–H_2O$ [76]; $MgCl_2–NaNO_3–H_2O$ [77]; $SrO–As_2O_5–H_2O$; $PbO–As_2O_5–H_2O$ [78]; Fe–Ni–P [79]; $HCl–S_2Cl_2$ [80]; $H_2O–CO_2–NH_3$ [81]; $K_2CO_3–KHCO_3–H_2O$ [82]; Fe–Zr [83];

[64] H. D. K. Drew, F. W. Pinkard, W. Wardlaw, and E. G. Cox, *J.*, 1932, 1004; *A.*, 562.

[65] H. D. K. Drew, *ibid.*, p. 2328; *A.*, 1101.

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Fe–Co–W [84]; Fe–Co–Mo [85]; NH_3–H_2S [86]; Na_2SiO_3–NaF [87]; Fe–C–O_2 [88]; systems SiO_2, CaO, and Al_2O_3 with C [89]; Na_2O–B_2O_3–H_2O [90]; Na_2SO_4–$Al_2(SO_4)_3$–H_2O [91]; $Mg(IO_3)_2$–$NaIO_3$–H_2O; $NaIO_3$–KIO_3–H_2O; KIO_3–KCl–H_2O; KIO_3–K_2SO_4–H_2O [92]; KIO_3–KNO_3–H_2O; $Ca(IO_3)_2$–$NaIO_3$–H_2O [93]; $KMnO_4$–KBF_4–H_2O [94]; $Pb(NO_3)_2$–$(Na,K,Ag,Tl)NO_3$ [95]; $CdCl_2$–KCl–H_2O [96]; $CdBr_2$–KBr–H_2O [97]; $Mg(NO_3)_2$–H_2O [98]; Na_2SO_4–H_2SO_4–H_2O [99]; $LiNO_3$–$TlNO_3$ [1]; CaO–Na_2O–Al_2O_3 [2]; SiO_2–ZnO–Al_2O_3 [3]; Ag–Cu–Zn [4]; MgO–CO_2–H_2O [5]; K_2CO_3–NH_3–H_2O [6]; $ZnSO_4$–NH_3–H_2O [7]; $CuCl_2$–LiCl–H_2O and $NiCl_2$–LiCl–H_2O [8]; $CoCl_2$–LiCl–H_2O [9]; $CuSeO_4$–H_2SeO_4–H_2O [10]; $La_2(SeO_4)_3$–H_2O [11]; $Pr_2(SeO_4)_3$–H_2O [12]; Ni–Zn [13]; $KReO_4$–H_2O [14]; $NaNO_2$–KNO_2 [15]; KF–AlF_3; LiF–AlF_3 [16]; $Ca(ClO_3)_2$–H_2O [17];

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[12] *Idem*, *ibid.*, p. 2410; *A.*, 1083.

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$KCl-PbCl_2-H_2O$ [18]; $KNO_3-NH_4NO_3-H_2O$ [19]; $CuSO_4-CoSO_4-H_2O$ [20]; carbamide-$H_2O_2-H_2O$ [21]; Al–Mg–Si [22]; Al–Mg–Cu [23]; Al–Cu–Si [24]; Al–Cu–Fe [25]; $HgBr_2-KBr-H_2O$ [26]; $MgO-MgCl_2-H_2O$ [27]; $NiSO_4-CaSO_4-H_2O$ [28]; Fe–C–Si [29]; $PbO-SiO_2$ [30]; Fe–Co–C [31]; Fe–Co–Cr [32]; $Fe-Fe_3C-FeS$ [33]; $KCl-NaCl-H_2O$ [34]; $MnSiO_3-Fe_2SiO_4$; $FeS-Fe_2SiO_4$ [35]; $CaCl_2-MgCl_2-H_2O$ [36]; $(NH_4)_2SO_4-Th(SO_4)_2-H_2O$ [37]; $MnSO_4-Th(SO_4)_2-H_2O$ [38]; $AgNCS-NH_3-H_2O$ [39]; $AgNCS-NaNCS-H_2O$; $AgNCS-KNCS-H_2O$; $AgNCS-NH_4NCS-H_2O$ [40]; $CaCl_2-Ca(NO_3)_2-H_2O$; $CaCl_2-Ca(ClO_3)_2-H_2O$; $SrCl_2-Sr(NO_3)_2-H_2O$; $KNO_3-Pb(NO_3)_2-H_2O$ [41]; $Na_2O-CaO-B_2O_3-SiO_2$ [42]; $K_2SiO_3-Na_2SiO_3-SiO_2$ [43]; $NaNO_3-KNO_3-Pb(NO_3)_2$.[44]

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[41] W. F. Ehret, *J. Amer. Chem. Soc.*, 1932, **54**, 3126; *A.*, 1091.

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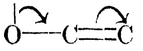
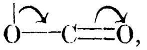
H. BASSETT.

ORGANIC CHEMISTRY.

PART I.—ALIPHATIC DIVISION.

Radicals and Ions.

Electropositive and Electronegative Character.—Great interest attaches to the determination of the relative electro-positivity and -negativity of organic radicals owing to the important influence which small differences in polarity can exert on the course of numerous reactions. An attempt has been made in a recent paper to place a series of alkyl and aryl radicals in the order of relative negativity by observing the behaviour of unsymmetrical mercury dialkyls with hydrogen chloride.[1] It is assumed that the group R′ which first dissociates from mercury and combines with the hydrogen ion in solution to form the hydrocarbon R′H according to the reaction: $R'HgR + HCl \longrightarrow R'H + HgRCl$, is the more electronegative of the two radicals; that is to say, it has the greater attraction for electrons and the greater tendency to split off as a negative ion by capturing the electron pair joining it to the metal. The order of increasing negativity amongst the radicals examined is the following: $CH_2Ph{\cdot}CH_2 < CH_2Ph < n\text{-}C_7H_{15} < n\text{-}C_4H_9 < C_3H_7 < C_2H_5 < CH_3 < m\text{-}C_6H_4Cl < o\text{-}C_6H_4Cl < p\text{-}C_6H_4Cl < C_6H_5 < m\text{-}CH_3{\cdot}C_6H_4 < p\text{-}CH_3{\cdot}C_6H_4 < o\text{-}CH_3{\cdot}C_6H_4 < \alpha\text{-naphthyl} < o\text{-}MeO{\cdot}C_6H_4 < p\text{-}MeO{\cdot}C_6H_4 < CN$, and it is seen that the order of the alkyl groups, relative to one another, is that which has been hitherto accepted (*iso*-groups are less negative than the corresponding *n*-groups, and *tert.*-groups less negative still), while amongst aryl radicals examined the tolyl and methoxy-radicals are more negative than phenyl, and the chlorophenyl radicals less so.

Certain of the broader considerations relating to the classification of groups are reviewed by R. Robinson in discussing the mechanisms of organic reactions.[2] Ordinarily the electropositiveness or negativeness of radicals is viewed in relation to hydrogen, which is arbitrarily taken as the standard for comparison. Then R in R·X is considered to be electropositive or electronegative according as X receives or loses electrons (by induction or by electromeric change) when H·X is transformed into R·X. In this way alkyl groups are always electropositive and NO_2, CO, CO_2Et, and CN are always electronegative, but it is evident that these designations cannot be applied to those virtually amphoteric atoms or groups which produce inductive and electromeric effects in opposite directions, unless there is some knowledge as to the importance of these effects or of their relative magnitude. Unsaturated radicals like vinyl and phenyl, although statically nearly always electropositive in character, are electronegative in relation to the corresponding saturated system; moreover, owing to structural flexibility and powers of co-operation in electromeric displacements which these groups display, no general electrical character can be assigned to them. Atoms possessing unshared electrons (N, O, Cl) and groups terminating in these atoms exercise generally a negative inductive effect (Cl $\longleftarrow$, O $\longleftarrow$, etc.) and are electronegative, but this can only be stated with certainty in the absence of electromeric transformations: indeed, where the electromeric displacements of the atom lead normally to reaction, *e.g.*, when the atom or group occurs in systems such as  $O—C{=}C$ or  $O—C{=}O$, the inductive effect acts by opposing or reversing the electromeric effect. The group NH_2 (not NR_2) is electronegative in $NH_2{\cdot}CH_2{\cdot}CH_3$ (dipole $\overset{\delta-}{N}—\overset{\delta+}{C}$), but in NH_2Ph, and even more so in $NH_2{\cdot}COR$, the action of the phenyl group is probably sufficient to reverse the polarity (dipole $\overset{\delta+}{N}—\overset{\delta-}{C}$). Chlorine on the other hand is always electronegative, but to a smaller degree when it is linked to an unsaturated group, especially if this is kationoid.

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The high reactivity of organo-magnesium compounds is to be attributed to the tendency towards separation of negatively charged alkyl groups (the tendency of the metal to assume kationoid functions not being thereby opposed) which, possessing only feeble affinity for their charge, act as energetic anionoid reagents. The alkyl groups of alkyl halides, of alkyl sulphates and of all esters, on the other hand, tend to separate as positively charged ions of kationoid reactivity, thus assisting the halogen atom to form a stable halide ion.[3]

Radical Transformations.—Many of the simpler transformations and isomerisations of organic chemistry can be interpreted as actually occurring by the transfer of H^+, H^-, Me^-, or electron pairs from one position to another within an organic kation produced by the separation of an electronegative group, although the reason for these changes is not always plain to see. Thus reactions such as the dehydration of *iso*butyl alcohol to yield *n*-butylenes in addition to the expected *iso*butylene, or of *tert.*-butyl alcohol to give mainly rearrangement products in any reaction in which hydroxyl is removed, can be summarised as due to the series of changes shown in (*a*)—a series which is analogous to that usually considered to be responsible for the well-known anionotropic isomerisation of allylic or propenoid compounds, shown in (*b*) :

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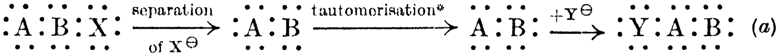
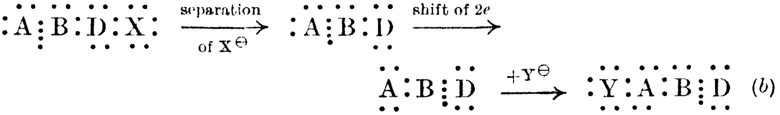
[3] It is doubtful whether the Würtz reaction, when appearing in competition with organo-magnesium halide formation in the Grignard reaction, can be formulated as simply as $\overset{-}{R}-\overset{++}{Mg}{\cdot}\overset{-}{Br}+\overset{+}{R}-\overset{-}{Br}\longrightarrow R-R+\overset{++--}{MgBr_2}$ in view of the lack of interaction between these two types of organo-halide when heated together (see p. 101).



(*a*)

* Shift of electron pair together with the atom or group which it holds.



(*b*)

The relationship between various well-known "abnormal" reactions of organic chemistry is discussed on these lines by F. C. Whitmore.[4]

Organo-metallic Compounds.

(Continued from *Ann. Reports*, 1928, **25**, 92.)

The papers which have appeared in this section since the last Report are so numerous that reference can be made to only a small proportion of them.

Metal Alkyls.—Lithium alkyls, LiR, which were originally prepared by the action of lithium on mercury dialkyls, have been shown to be obtainable by the action of the metal directly on alkyl and aryl halides in ether or benzene.[5] Ethyl-lithium reacts with diethylthallium chloride to yield a true thallium trialkyl, $TlEt_3$,[6] and by the action of gallium tribromide on methylmagnesium bromide in ethereal solution the etherate of trimethylgallium, $GaMe_3,Et_2O$, is obtainable.[7] Tetraethylgermanium has been found to yield on bromination triethylgermanium bromide, $GeEt_3Br$, and from this compound the tri- and di-ethyl oxides and imines of germanium, $(GeEt_3)_2O$, $GeEt_2O$, $(GeEt_3)_2NH$, and $GeEt_2{:}NH$, and various other alkyl derivatives of germane and digermane have been directly or indirectly obtained.[7] Magnesium dialkyls and diaryls can be obtained smoothly by the action of magnesium on mercury dialkyls and diaryls in ether. Contrary to earlier observations, the latter compounds are soluble in ether.[8]

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[6] H. P. A. Groll, *ibid.*, 1930, **52**, 2998; *A.*, 1930, 1302.

[7] C. A. Kraus and E. A. Flood, *ibid.*, 1932, **54**, 1635; E. A. Flood, *ibid.*, p. 1663; *A.*, 606.

Observations of the thermal decomposition of sodium and potassium methyls indicate that the reaction proceeds ultimately according to the equation: $8M{\cdot}CH_3 = 6CH_4 + M_2C_2 + 6M$. Methylsodium is regarded as the salt of a weak acid, the anion of which suffers the fundamental change: $4CH_3^- \longrightarrow 3CH_4 + C^{----}$, owing to the capture of protons by some of the methide ions at the expense of others. The stripped quadrivalent ions do not, however, persist, for what is found is the acetylide ion, which is formed presumably by the combination of pairs of quadrivalent ions with loss of electrons: $2C^{----} \longrightarrow C{\vdots}C^{--} + 6e$.[9] In the spontaneous decomposition of ethylsodium at the ordinary temperature, the main reaction can be represented as due to the transfer of a proton from one ethide ion of every pair to the other, thus effecting the change $2NaEt \longrightarrow Na_2C_2H_4 + C_2H_6$; at 90—100°, however, the ethide ions appear for the most part to lose a proton and an electron pair (hydride ion), the main decomposition being then expressed by the scheme $NaEt \longrightarrow NaH + C_2H_4$, although some ethane accompanies the ethylene.[10] Study of the thermal decomposition of diethylmercury and tetraethyl-lead yields the interesting result that when decomposition is effected in ethylene at 250—300°, the ethylene polymerises, the initial reaction being most probably between the latter substance and the ethyl radicals, $C_2H_5 + 2C_2H_4 = C_4H_9 + C_2H_4$, followed by $C_4H_9 + 2C_2H_4 = C_6H_{13} + C_2H_4$, the radicals being ultimately eliminated by mutual interaction or owing to contact with exposed surfaces.[11]

Grignard Reagents.—There now remains little doubt that in ordinary ethereal Grignard solutions equilibria always occur in accordance with the scheme:

$$2MgRHal \rightleftharpoons MgR_2 + MgHal_2$$ [12, 13]

The part played by the ether in the formation of these solutions is due to its solvent power, not only for the organo-metallic compounds, but also for the magnesium halides.[12] The position of equilibrium depends on the nature of the halide: thus, for a number of simple alkyl bromides and iodides the equilibrium is displaced to the right with increase in weight of the alkyl group, and substitution of bromide for iodide has little effect; with chlorides, the establishment of equilibrium occurs very slowly and is complicated by the separation of magnesium chloride.[14, 15] Progress of the reaction in the backward direction has been demonstrated in the case of phenylmagnesium halides [13, 14] and it has been found that a very small amount of magnesium halide is sufficient to initiate reaction between triphenylmethyl and magnesium, and to bring about, owing to the continuous regeneration of magnesium halide, complete conversion into the Grignard reagent thus: $2Ph_3C + Mg + MgX_2 \longrightarrow 2CPh_3{\cdot}MgX \rightleftharpoons (CPh_3)_2Mg + MgX_2$.[16]

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[8] W. Schlenk, jun., *Ber.*, 1931, **64**, [*B*], 736; *A.*, 1931, 719. Compare H. Gilman and R. E. Brown, *J. Amer. Chem. Soc.*, 1930, **52**, 5045; *A.*, 1931, 206.

[9] W. H. Carothers and D. D. Coffman, *ibid.*, p. 1254; *A.*, 1930, 757.

[10] *Idem*, *ibid.*, 1929, **51**, 588; *A.*, 1929, 433.

[11] H. S. Taylor and W. H. Jones, *ibid.*, 1930, **52**, 1111; *A.*, 1930, 757.

[12] W. Schlenk and W. Schlenk, jun., *Ber.*, 1929, **62**, [*B*], 920; *A.*, 1929, 687. An alternative representation, $R_2Mg,MgHal_2 \rightleftharpoons MgR_2 + MgHal_2$, is considered less likely to be correct.

[13] H. Gilman and R. E. Fothergill, *J. Amer. Chem. Soc.*, 1929, **51**, 3149; *A.*, 1929, 1432.

Both the alkylmagnesium halides and the magnesium alkyls which are present in the Grignard solutions are active reagents, and doubtless the two types of reaction product, *viz.*, $R_3C{\cdot}O{\cdot}MgHal$ and $R_3C{\cdot}O{\cdot}Mg{\cdot}O{\cdot}CR_3$ which are produced by the action of Grignard solutions on aldehydes and ketones, owe their respective origins to the two types of compound.[17] The ratio $MgR_2/(MgR_2 + MgRX)$, which can be determined experimentally with some precision,[17] is considerably modified (increased or decreased) when the magnesium employed is alloyed or mixed with copper, or when metallic zinc or salts such as mercuric chloride are added to the reactants. But the addition of the latter substances has usually another effect, *viz.*, to suppress to a smaller or greater extent the formation of Grignard reagents and correspondingly to favour the Würtz reaction (yielding hydrocarbons $R{\cdot}R$) which commonly competes therewith.[15, 18] Copper–magnesium alloy, like iodine, forms an excellent catalyst for starting the Grignard reaction, but in most of the instances examined the presence of either substance in significant proportion seriously reduces the yield of Grignard reagent and correspondingly enhances the yield of Würtz reaction products.[19] The ratio $R{\cdot}R/(MgR_2 + MgRX)$ is thus increased by the added substances, but in the case of the Grignard reagent from allyl bromide is notably decreased (from 72% to 6%) by the influence of copper. There is no reason to think that the Würtz reaction as it

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[14] W. Schlenk, jun., *Ber.*, 1931, **64**, [*B*], 734; *A.*, 1931, 718.

[15] G. O. Johnson and H. Adkins, *J. Amer. Chem. Soc.*, 1932, **54**, 1943; *A.*, 728. The proportion of active reagent present as MgR_2 is given as 6% for EtI and 84% for BuCl.

[16] W. E. Bachmann, *ibid.*, 1930, **52**, 4412; *A.*, 1931, 79.

[17] W. Schlenk, jun., *Ber.*, 1931, **64**, [*B*], 736; *A.*, 1931, 719.

[18] G. O. Johnson and H. Adkins, *J. Amer. Chem. Soc.*, 1931, **53**, 1520; *A.*, 1931, 719.

[19] H. Gilman and E. A. Zoellner, *ibid.*, p. 1581; *A.*, 1931, 719.

occurs here results from the action of either type of active Grignard reagent on the original alkyl halide employed, since both types of reagent have been found to be quite unreactive towards the corresponding alkyl halides (allyl is an exception).[15] Grignard reagents can, however, be converted in smaller or greater measure into products of the Würtz–Fittig type by the direct action of various heavy-metal salts, and it is reported that when an arylmagnesium halide is added to a suspension of silver bromide a silver aryl is first obtained which decomposes into silver and diaryl when the reaction mixture is boiled.[20]

Organo-magnesium halides can in some cases be prepared free from ether by employing benzene as the medium in the Grignard reaction,[21] or by avoiding the use of a solvent altogether.[22] They may also be formed and undergo reaction *in situ* when a ketone or ester replaces the solvent; in this case, however, exchange of alkyl groups between the reactants may occur in presence of the metal.[21] Certain of the lower alkylmagnesium halides can be distilled (sublimed) in a stream of ether, but there is nothing to show whether the organo-halides distil as such rather than as the mixture in equilibrium therewith: in high vacuum distillations magnesium alkyls are obtained.[23]

The reactive properties of Grignard reagents have been further studied. An important property which has received a large amount of attention is the reductive action which manifests itself when the reagents react with certain aldehydes and ketones. Aldehydes and ketones which themselves contain branched chains or are employed with organo-magnesium compounds containing branched chains often become more or less completely reduced to the corresponding primary or secondary alcohols—a circumstance which seriously limits the usefulness of the Grignard method for synthesising secondary or tertiary carbinols but affords in certain cases a convenient means of reducing the aldehydes and ketones concerned.[24] Although this reducing action appears to be directly related to the complex character of the alkyl groups present in the reactants, no definite and exact correlation has been possible between the amount of reduction obtainable and the degree of complexity or the incidence of the complex groups in one or other (or both) reactants.[25] It appears to be the case, however, that for the synthesis of tertiary aliphatic carbinols containing both straight and branched alkyl groups, it is best to employ (α-)branched-chain ketones and magnesium *n*-halides. Whether or no each of the organo-magnesium compounds present in the Grignard reagent can, without equilibration, effect reduction has not yet been satisfactorily determined, but it has been found that di*iso*butylmagnesium, which constitutes 75% of the reagent prepared from *iso*butyl bromide, reduces benzophenone to benzyhydrol to the extent of at least 64%, and the Grignard reagent before separation effects reduction to the extent of 84%.[26]

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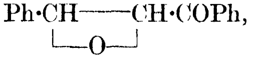
[20] J. H. Gardner and P. Borgstrom, *J. Amer. Chem. Soc.*, 1929, **51**, 3375; *A.*, 1930, 76.

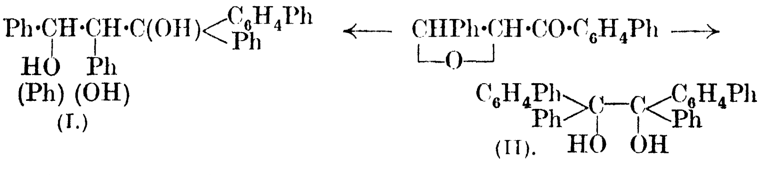
[21] W. Schlenk, jun., *Ber.*, 1931, **64**, [*B*], 739; *A.*, 1931, 718.

[22] H. Gilman and R. E. Brown, *J. Amer. Chem. Soc.*, 1930, **52**, 5045; *A.*, 1931, 206.

[23] *Idem, ibid.*, p. 4480; *A.*, 1931, 78; *Rec. trav. chim.*, 1929, **48**, 1133; *A.*, 1930, 76.

[24] J. B. Conant and A. H. Blatt, *J. Amer. Chem. Soc.*, 1929, **51**, 1227; *A.*, 1929, 675.

Kohler and his collaborators, in examining the behaviour of keto-oxido-compounds towards Grignard reagents, showed that benzylideneacetophenone oxide,  $\underset{\llcorner\!\!-\!O\!-\!\!\lrcorner}{Ph\cdot CH\text{——}CH\cdot COPh}$, with phenylmagnesium bromide yields triphenylcarbinol, $Ph_3C\cdot OH$.[27] Here the first step is probably the scission of the benzoyl group as benzophenone, which is then transformed into the carbinol. With most keto-oxido-compounds a similar result is obtained and many relatively heavily phenylated esters suffer fission under the action of the Grignard reagent. With benzylidene-*p*-phenylacetophenone oxide, however, two reactions occur, in one of which both the ketone group and the oxide ring are attacked, yielding (I) or its isomeride, and in the other a preliminary scission of phenyl *p*-diphenylyl ketone is apparently followed by the reduction of the latter to a pinacol (II).[28]



(I.)

(II).

β-Substituted allyl bromides, the structure of which permits of anionotropic change, can react with Grignard reagents to give isomeric olefins (III and IV), which are derived by combination of the alkyl group from the reagent with the tautomeric forms of the unsaturated kation; [29] in other cases they react to give hydrocarbons (V and VI), which appear to owe their origin to a functional exchange between the reactants: $R{\cdot}CH{:}CH{\cdot}CH_2Br + MgEtBr \longrightarrow R{\cdot}CH{:}CH{\cdot}CH_2{\cdot}MgBr + EtBr$.[30] The Würtz reaction is found to accompany the latter type of reactivity, and both here,[30] and where the substituted allyl bromides react directly with magnesium,[31] the coupling of the hydrocarbon radicals may take place in one or more of three ways yielding substituted hexadienes (VII, VIII, and IX).

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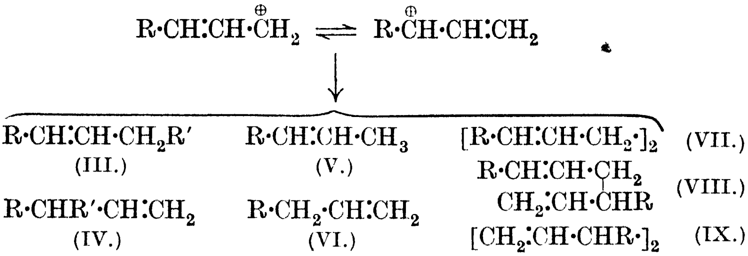
[25] A. H. Blatt and J. F. Stone, jun., *J. Amer. Chem. Soc.*, 1932, **54**, 1495; *A.*, 598.

[26] C. R. Noller, *ibid.*, 1931, **53**, 635; *A.*, 1931, 473.

[27] E. P. Kohler, N. K. Richtmyer, and W. F. Hester, *ibid.*, p. 205; *A.*, 1931, 354.

[28] E. Bergmann and H. A. Wolff, *ibid.*, 1932, **54**, 1644; *A.*, 616.

[29] C. Prévost and J. Daujat, *Bull. Soc. chim.*, 1930, [iv], **47**, 588; *A.*, 1930, 1158.



$$R{\cdot}CH{:}CH{\cdot}\overset{\oplus}{C}H_2 \rightleftharpoons R{\cdot}\overset{\oplus}{C}H{\cdot}CH{:}CH_2$$

$$\downarrow$$

$$\begin{array}{ccll}
R{\cdot}CH{:}CH{\cdot}CH_2R' & R{\cdot}CH{:}CH{\cdot}CH_3 & [R{\cdot}CH{:}CH{\cdot}CH_2{\cdot}]_2 & \text{(VII.)} \\
\text{(III.)} & \text{(V.)} & R{\cdot}CH{:}CH{\cdot}CH_2 & \\
 & & \quad | & \text{(VIII.)} \\
R{\cdot}CHR'{\cdot}CH{:}CH_2 & R{\cdot}CH_2{\cdot}CH{:}CH_2 & CH_2{:}CH{\cdot}CHR & \\
\text{(IV.)} & \text{(VI.)} & [CH_2{:}CH{\cdot}CHR{\cdot}]_2 & \text{(IX.)}
\end{array}$$

Grignard reagents react with arsenic trichloride and antimony trichloride to give trialkylarsines[32] and trialkylstibines respectively, and with α-*tert*.-amino-nitriles to yield amino-ketones in addition to amino-hydrocarbons in which the nitrile group has been replaced by the alkyl radical of the Grignard reagent:[33]

$$NR^3R^4{\cdot}CR^1R^2{\cdot}CN + MgR^5X \begin{array}{l} \nearrow NR^3R^4{\cdot}CR^1R^2{\cdot}COR^5 \\ \searrow NR^3R^4{\cdot}CR^1R^2R^5 + MgXCN \end{array}$$

Reference may also be made to new studies of the action of Grignard reagents on dialkylamides, $R^1{\cdot}CO{\cdot}NR^2R^3$,[34] α-cyano-esters,[35] carbonic esters[36] and sulphonyl chlorides.[37]

Compounds of Boron.

Boron trifluoride reacts with simple organic compounds of different types to give addition compounds, and as early as 1891 Patein obtained a solid product from acetonitrile and boron trifluoride. The manner of formation and the constitution of these compounds have recently been studied independently by different workers[38] and it is now apparent that, when boron trifluoride is passed into fatty acids, the esters of fatty (and certain other) acids, ethers, amides, and nitriles, simple addition products are quite frequently produced.

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[30] C. Prévost, *Bull. Soc. chim.*, 1931, [iv], **49**, 1372; *A.*, 1932, 41.

[31] C. Prévost and G. Richard, *ibid.*, p. 1368; *A.*, 1932, 40.

[32] W. J. C. Dyke and W. J. Jones, *J.*, 1930, 2426, 463; *A.*, 1931, 77; 1930, 587.

[33] T. S. Stevens, J. M. Cowan, and J. MacKinnon, *ibid.*, 1931, 2568; *A.*, 1931, 1404.

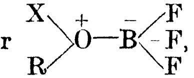
[34] (Mlle.) M. Montagne, *Ann. Chim.*, 1930, [x], **13**, 40; *A.*, 1930, 460; *Compt. rend.*, 1931, **192**, 1111; *A.*, 1931, 831; S. P. Ti, *ibid.*, 1930, **191**, 943; *A.*, 1931, 77.

[35] A. Mavrodin, *ibid.*, 1930, **191**, 1064; 1931, **192**, 363; *A.*, 1931, 205, 471.

[36] D. Ivanov, *ibid.*, 1929, **189**, 830; 1931, **193**, 773; *A.*, 1930, 61; 1932, 43.

[37] H. Gilman and R. E. Fothergill, *J. Amer. Chem. Soc.*, 1929, **51**, 3501; *A.*, 1930, 462.

Esters such as methyl and ethyl formate, methyl, ethyl and propyl acetate, ethyl propionate and methyl benzoate, give distillable liquids or solids which have the general constitution $R'{\cdot}CO_2R'',BF_3$; acetic acid and propionic acid yield liquids which are distillable with some decomposition under reduced pressure, and appear to have the composition $(CH_3{\cdot}CO_2H)_2,BF_3$ and $(Et{\cdot}CO_2H)_2,BF_3$ respectively; acetonitrile yields a distillable solid product, $MeCN,BF_3$, and acetic anhydride a solid Ac_2O,BF_3. Methyl and ethyl alcohols give with boron trifluoride solutions of high conductivity, due to the formation of addition compounds, $R{\cdot}OH,BF_3$, which ionise to yield hydrion and the corresponding complex organic ions; the higher alcohols, however, suffer decomposition to hydrocarbons. Anisole and phenetole give undistillable liquid addition products with boron trifluoride.

All the above compounds appear to be capable of formulation in the manner  $\begin{smallmatrix}X\\R\end{smallmatrix}{>}\overset{+}{O}{-}\overset{-}{B}{<}\begin{smallmatrix}F\\F\\F\end{smallmatrix}$, in which the link between boron and oxygen is a co-ordinate link or semipolar double bond. The addition product of boron trifluoride with alcohol has been used as a catalyst in converting acetylene into acetals[39] and in the esterification of acetic and propionic acids with various alcohols; in the former case the reaction is assumed to be due to the addition of the ions of the complex to the hydrocarbon:

$$CH{:}CH + 2H^{\oplus} + 2[RO{\rightarrow}BF_3]^- \longrightarrow CH_3{\cdot}CH(OR{\rightarrow}BF_3)_2 \longrightarrow CH_3{\cdot}CH(OR)_2 + 2BF_3$$

Boron trichloride[40] reacts vigorously with methyl and ethyl alcohols at low temperatures to give quantitative yields of low-melting, volatile alkoxy-compounds, $BCl_2{\cdot}OR$, $BCl(OR)_2$, and $B(OR)_3$ (R = Me or Et); these are readily hydrolysed by water or alcoholysed (if they contain chlorine) with excess of alcohol. Boron trichloride and the monoalkoxy-derivative $BCl_2{\cdot}OR$ react with methyl or ethyl ether even at − 80° to form the additive compounds, BCl_3,R_2O and $(BCl_2{\cdot}OR)_2,R_2O$, but the di- and tri-alkoxy-derivatives, $BCl(OR)_2$ and $B(OR)_3$, do not react therewith even at 100°. The addition product BCl_3,Et_2O reacts vigorously with alcohol at − 40° to yield the compound $(BCl_2{\cdot}OEt)_2,Et_2O$, which readily decomposes into the compounds BCl_3,Et_2O and $BCl(OEt)_2$. The thermal decomposition of these substances has been studied.

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[38] H. Bowlus and J. A. Nieuwland, *J. Amer. Chem. Soc.*, 1931, **53**, 3835; *A.*, 1931, 1404; G. T. Morgan and R. Taylor, *Chem. and Ind.*, 1931, 869; *J.*, 1932, 1497; *A.*, 1931, 1404; 1932, 728.

[39] J. A. Nieuwland, R. R. Vogt, and W. L. Foohey, *J. Amer. Chem. Soc.*, 1930, **52**, 1018; *A.*, 1930, 745; H. D. Hinton and J. A. Nieuwland, *ibid.*, 1930, **52**, 2892; 1932, **54**, 2017; *A.*, 1930, 1160; 1932, 728.

[40] E. Wiberg and W. Sütterlin, *Z. anorg. Chem.*, 1931, **202**, 1, 22, 31, 37; *A.*, 1932, 258.

Tri-*tert.*-butylboron, which has been obtained by the action of boron trifluoride on *tert.*-butylmagnesium chloride in ether, is converted on oxidation into *tert.*-butylboric acid. Tri-*sec.*-propylboron resembles the *tert.*-butyl derivative.[41]

Olefinic, Di-olefinic, and Acetylenic Compounds.

Additive Reactions.—The various factors which enter into consideration in connexion with the problems of orientation in olefinic and polyolefinic additions were referred to in last year's Report. The new work on this subject refers mainly to the influence of the groups present in unsaturated substances on the orientation of their addition products, but it is becoming increasingly evident that the influence of the reaction conditions (especially conditions relating to solvent and to catalytic influences) is of considerable importance in determining the course of reaction in certain types of addition.

All the evidence available from the literature goes to show that in the addition of an unsymmetrical molecule XY to an ethylenic hydrocarbon $R^1CH{:}CHR^2$, the ultimate distribution of the addendal components X and Y, is largely determined by the influence of the groups R^1 and R^2 on the direction of olefinic polarisation. In general both of the compounds $R^1{\cdot}CHX{\cdot}CHYR^2$ and $R^1{\cdot}CHY{\cdot}CHXR^2$ are likely to be formed, but as yet there is little in the way of accurate quantitative evidence to show how completely the results of addition can be correlated with the character of the groups R^1 and R^2, or how far the observed orientation in given examples is independent of the conditions of reaction and of the nature of the addendum XY. With respect to the manner in which alkyl groups influence the orientation at a double bond R. Robinson[42] has pointed out that it is doubtful whether the inductive displacements which are usually attributed to alkyl groups (represented by $CH_3\rightarrow$, $C_2H_5\rightarrow$, etc.) can lead directly to reactivity, the reason being that only unshared electrons can take part in co-valency formation, and inductive displacements do not appear to modify the extent of sharing in a bond from the point of view of the numbers of quantised electrons associated with the atoms in question, although they admittedly disturb the sharing electrostatically. Rather must reaction be preceded by a degree of electronic polarisation (symbolised by $C\overset{\curvearrowright}{=}C$) in which electrons actually dissociate themselves from one of the carbon atoms and become free to be shared with external atoms—thus providing the means by which anionoid olefinic molecules react.

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[41] E. Krause and P. Nobbe, *Ber.*, 1931, **64**, [*B*], 2112; *A.*, 1931, 1280.

[42] "Outline of an Electrochemical (Electronic) Theory of the Course of Organic Reactions," p. 16.

The important effect of alkyl substitution would seem to be clearly shown by a series of additions to Δ^{α}-, Δ^{β}-, and Δ^{γ}-unsaturated acids recently carried out.[43] The extent to which the addition of hypochlorous acid to each of three isomeric hexenoic acids occurs in opposite directions is shown in the scheme :

$\mathrm{Me{\cdot}\mathbf{CH{:}CH}{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H}$
Cl......OH 95%.
OH......Cl 5%.

$\mathrm{Et{\cdot}\mathbf{CH{:}CH}{\cdot}CH_2{\cdot}CO_2H}$
Cl......OH 20%.
OH......Cl 80%.

$\mathrm{Pr^{\alpha}{\cdot}\mathbf{CH{:}CH}{\cdot}CO_2H}$
OH......Cl 100%.

Here on the basis of the order of inductive effects usually accepted for the lower alkyl groups (*viz.*, Pr>Et>Me>H), the orientations observed experimentally are completely in accord with expectation, provided it is assumed that the substitution of a carboxyl group in an alkyl group, as instanced by $\mathrm{{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H}$ and $\mathrm{{\cdot}CH_2{\cdot}CO_2H}$, does not diminish—or diminishes very slightly—the inductive effect of the alkyl group, and that the carboxyl group itself, when attached directly to an olefinic linkage, possesses little orienting influence compared with alkyl, or none at all.

Under the conditions of the above reaction and with hypochlorous acid as the addendum it is doubtless true that the orienting influence of a carboxyl group in the system $\mathrm{CH{:}CH{\cdot}CO_2H}$ is much smaller than that of even a methyl group.[44] But no *general* conclusion can be drawn from the above-cited facts as to the efficacy of the carboxyl group as an orienting influence, either in the case (*a*) represented by the group $\mathrm{{\cdot}CH{:}CH{\cdot}CO_2H}$, in which a conjugated system is present, or in the case (*b*) represented by the system $\cdot CH{:}CH\cdot[CH_2]_n\cdot CO_2H$, in which the carboxyl group is removed to a distance from the ethylenic centre. For in case (*a*) there is every probability that different addenda react in different ways: thus hypochlorous acid, being a reagent for the ethylenic linkage *per se*, and having no tendency to add *via* the carboxyl group, is probably comparatively little influenced by the latter in respect of the orientation assumed; but addenda such as the hydrogen halides, although these are also reagents for the ethylenic bond *per se*, appear to add preferably at the ends of the conjugated system, the addition being initiated by the attachment of the proton to carbonyl oxygen. Similarly in case (*b*) it has recently been argued [2,44a] that, although in examples such as the hydration of stearolic acid (X) [45] the observed orientation is improbably due to the influence of the carboxyl group, transmitted from atom to atom along the carbon chain,

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[43] G. F. Bloomfield and E. H. Farmer, *J.*, 1932, 2062; *A.*, 930.

[44] Comparisons (unpublished) made by the Reporter, together with Dr. Bloomfield and Mr. C. Hose, between the orientations assumed by the components of hypochlorous acid in the systems $\mathrm{Me{\cdot}CH{:}CH{\cdot}CO_2H}$, $\mathrm{Me{\cdot}CH{:}CMe{\cdot}CO_2H}$, $\mathrm{CH_2{:}CMe{\cdot}CO_2H}$, and $\mathrm{CH_2{:}CMe{\cdot}CO_2Et}$ show how important the influence of the methyl group can be, but also how materially the carboxyl group can affect the orientation.

$$CH_3\cdot[CH_2]_7\cdot C{\vdots}C\cdot[CH_2]_7\cdot CO_2H$$
2OH......2H (57·6%)
(X.) 2H......2OH (12·4%)

$$CH_2{:}CH\cdot[CH_2]_8\cdot CO_2H$$
Br......H (in toluene)
H......Br (in ether) (XI.)

yet it may be due to the transmission of this influence through the intervening space ("field effect"): but here a further complication enters, in that the medium may be such as to transmit the influence readily or to dissipate it—a state of affairs which has been considered to receive illustration in hydrogen bromide addition to Δ^{ι}-undecylenic acid (XI),[46] where the change from a toluene to an ether medium completely reverses the mode of addition. Whether or no the field effect has the importance thus attributed to it awaits future verification, but there are not wanting indications that the condition of the carboxyl group—ionised or un-ionised—can have a strong determining influence on orientation, so that it is quite improbable that an absolute mode of addition can usually be assigned to a mono-olefinic acid, irrespective of the experimental conditions and of the character of the unsymmetrical addendum.

Ammonia, methylamine, and diethylamine add readily to ethyl crotonate, giving the corresponding β-amino- or β-alkylaminobutyric esters.[47] Reaction proceeds at room temperature and liquid ammonia or alcoholic ammonia may be employed. In the case of ammonia ethyl ββ′-iminodibutyrate is also formed.

A study of the lactonisation of Δ^{α}- and Δ^{β}-unsaturated acids has

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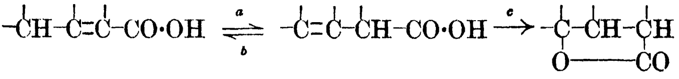
[44a] R. Robinson, "Outline of an Electrochemical (Electronic) Theory of the Course of Organic Reactions," p. 32.

[45] (Mrs.) G. M. Robinson and R. Robinson, *J.*, 1926, 2204; *A.*, 1926, 1024.

[46] J. Walker and J. S. Lumsden, *ibid.*, 1901, **79**, 1191.

[47] K. Morsch, *Monatsh.*, 1932, **60**, 50; *A.*, 600.

shown that all acid–γ-lactone systems can be interpreted in one general scheme :[48]



$$-\overset{|}{C}H-\overset{|}{C}=\overset{|}{C}-CO\cdot OH \underset{b}{\overset{a}{\rightleftharpoons}} -\overset{|}{C}=\overset{|}{C}-\overset{|}{C}H-CO\cdot OH \xrightarrow{c} -\underset{\displaystyle O}{\overset{|}{\underset{|}{C}}}-\overset{|}{C}H-\underset{\displaystyle CO}{\overset{|}{\underset{|}{C}}}H$$

γ-lactone

Lactonisation represents an addition reaction in which the components of the carboxyl group, H and R·CO·O, become attached to the olefinic centre; consequently, analogies are to be expected with other additions in which the addendum is of the type HX, but here special limitations are imposed by the bound condition of the anionic component of the addendum. Originally R. Fittig and his collaborators had maintained that only Δ^{β}-unsaturated acids and allylacetic acid (the only Δ^{γ}-acid then known) could be converted by boiling 50% sulphuric acid into γ-lactones. This generalisation, however, is incorrect, since simple Δ^{α}-acids give appreciable quantities of lactone under Fittig's experimental conditions. The variations between different systems can be attributed to differences in the ratio of the velocity of tautomeric change (*a* and *b*) to that of ring closure (*c*). Three, possibly four, types of acid can be distinguished : (i) those in which both changes are slow, but lactonisation is much faster than tautomeric change (acids with one γ-alkyl group and no β-alkyl substituent); (ii) those in which lactonisation is fast and tautomeric change slow (acids with two γ-alkyl substituents); (iii) those in which tautomeric change is faster than lactonisation (acids with one γ- and one β-substituent); (iv) (?) those in which tautomeric change is fast and irreversible in the direction $\beta\gamma \longrightarrow \alpha\beta$, no lactonisation being possible (acids without γ-substituents). No evidence of the re-formation of a Δ^{β}-acid from a simple lactone by treatment with sulphuric acid or by prolonged heating has been discovered : consequently lactonisation is formulated as irreversible, but the change, lactone $\longrightarrow$ Δ^{α}-acid, appears to be possible in more complicated systems such as lactonic acids of the paraconic type.

The manner of addition of hydrogen chloride to conjugated olefin-acetylenes resembles that of hydrogen bromide to the conjugated butadienes.[49] In the latter case the hydrogen of the addendum always attaches itself (so far as existing evidence shows) as a proton to a terminal carbon atom of the chain, whilst the bromide ion becomes linked at either the second or fourth carbon atom. With vinylacetylene (XII) and the *iso*propenyl-, *iso*butenyl- and *cyclo*hexenyl-acetylenes represented by formulæ (XIII), (XIV), and (XV), the hydrogen component of the addendum attaches itself to the terminal acetylenic carbon atom, whilst the chlorine component becomes linked at the fourth carbon atom in the case of vinylacetylene, and at the second in the remaining instances.

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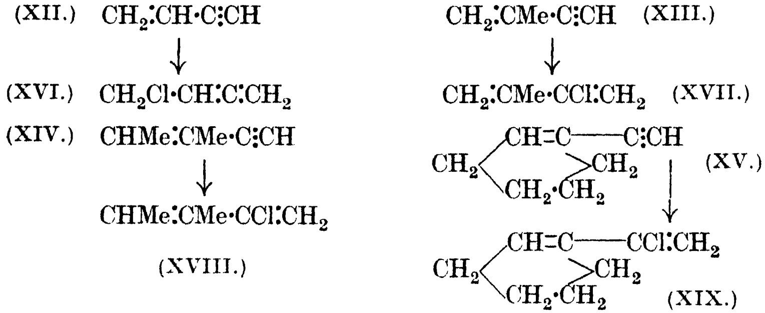
[48] R. P. Linstead, *J.*, 1932, 115; *A.*, 251.

[49] W. H. Carothers, G. J. Berchet, and A. M. Collins, *J. Amer. Chem. Soc.*, 1932, **54**, 4066; *A.*, 1231; W. H. Carothers and D. D. Coffman, *ibid.*, p. 4071; *A.*, 1232.



(XII.) $CH_2{:}CH{\cdot}C{\vdots}CH \longrightarrow$ (XVI.) $CH_2Cl{\cdot}CH{:}C{:}CH_2$

(XIII.) $CH_2{:}CMe{\cdot}C{\vdots}CH \longrightarrow$ (XVII.) $CH_2{:}CMe{\cdot}CCl{:}CH_2$

(XIV.) $CHMe{:}CMe{\cdot}C{\vdots}CH \longrightarrow$ (XVIII.) $CHMe{:}CMe{\cdot}CCl{:}CH_2$

(XV.) → (XIX.)

The formation of the allene derivative (XVI) is particularly interesting. This substance can be isolated as the major product under certain conditions of reaction, but in the presence of hydrogen chloride it undergoes isomerisation to β-chlorobutadiene so readily that the latter substance always constitutes part of the reaction product. Certain salts reinforce the catalytic effect of hydrogen chloride, and when cuprous chloride is present none of the allene derivative survives. β-Chlorobutadiene has been designated "chloroprene" in analogy with isoprene, and has been made the starting material for the production of synthetic rubber. Chloroprene adds a further molecule of hydrogen chloride, yielding αγ-dichloro-Δ^{β}-butene.

In the addition of hypochlorous acid to sorbic acid and to β-vinylacrylic acid the main influence of the carboxyl group is to decide which of the two double bonds of the conjugated system shall be attacked. The αβ-unsaturated centre becomes de-activated, and the anionic charge develops at the δ-carbon atom. Attachment of the chlorine component of the addendum then occurs at the δ-carbon atom in the manner :[50]

$$CH_3{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CO_2H \longrightarrow CH_3{\cdot}CHCl{\cdot}CH(OH){\cdot}CH{:}CH{\cdot}CO_2H$$
$$CH_2{:}CH{\cdot}CH{:}CH{\cdot}CO_2H \longrightarrow CH_2Cl{\cdot}CH(OH){\cdot}CH{:}CH{\cdot}CO_2H$$

Sorbic acid and its homologues of the series

$$R^1R^2C{:}CR^3{\cdot}CR^4{:}CR^5{\cdot}CO_2H$$

react with hydrogen in the presence of a platinum catalyst in different ways.[51] At room temperature and atmospheric pressure four types of addition take place, *viz.*, αβ-, αδ-, γδ-, and αβγδ-, the last of these representing unpreventable attack at both ethylenic centres simultaneously. The different acids of the series yield mixtures of the different types of addition product, but examination of the reaction mixtures after partial hydrogenation shows that hydrogenation follows a different course for each acid; the constitution of the conjugated compound (*i.e.*, the character of the substitution in the chain) appears definitely, therefore, to be reflected in the additive mode. It is found, however, that the figures representing the proportions of the various reduction products at the intermediate stages of reduction are by no means to be regarded as solely determined by, or affording a true measure of, the structural influences at work in the individual acids; for, although they are reproducible if the catalyst is freshly prepared from platinum oxide, when a less active (" aged ") catalyst is used the course of hydrogenation (in the case of sorbic acid at least) [52] becomes considerably changed. Thus the nature and extent of substitution in the butadiene chain is not, under the conditions of temperature and pressure employed, the sole, or apparently the most important, influence in determining the course of reaction. The substitutional or constitutive influence, with its activating or deactivating tendencies, appears to be superimposed on a specific catalytic influence which is capable of activating both unsaturated centres of the conjugated system simultaneously.

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[50] G. F. Bloomfield and E. H. Farmer, *J.*, 1932, 2072; *A.*, 930.

Striking observations respecting selective hydrogenation in the non-conjugated (diolefinic) linoleic acid series are due to T. P. Hilditch and E. C. Jones.[53] In hydrogenating the unsaturated glycerides contained in olive and cottonseed oils with a nickel–kieselguhr catalyst it is found that the linoleic groups are very largely converted into oleic and *iso*oleic groups before the latter are further hydrogenated; after the linoleo-glycerides have disappeared, steady increase in the total saturated acid commences, but development of fully saturated glycerides is relatively slow until the final stages of hydrogenation. Further it is found that trioleins (mixtures of oleic and *iso*oleic triglycerides) at first disappear much more rapidly than fully-saturated components are produced, indicating that a molecule of triolein, adsorbed by nickel, is desorbed as soon as a single oleic group has undergone hydrogenation. Thus direct transformation of molecules of triolein into tristearin at one and the same contact with the catalyst does not occur and a single unsaturated centre only is involved in each effective contact between catalyst and a triolein molecule; in this way the hydrogenation of different classes of unsaturated glycerides is definitely selective, the order of reduction being trioleins, di-oleo-compounds, and mono-oleo-compounds.

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[51] E. H. Farmer and R. A. E. Galley, *J.*, 1932, 430; *A.*, 365.

[52] *Idem*, *Nature*, 1933, **131**, 60.

[53] *J.*, 1932, 805; *A.*, 498.

Formation of Dimerides, Trimerides, and Tetramerides.—Olefins. To the list of dimerides and trimerides (including XX—XXIII below), the constitutions of which have been definitely established during the past three years, must now be added dimeric indene (XXIV).[54]

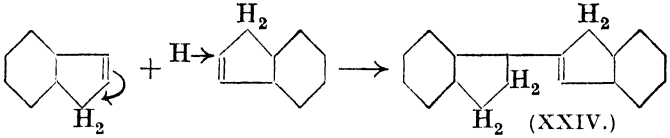
$$1.\ H_2\overset{\curvearrowleft}{C}{=}CMe_2 + H{\rightarrow}CH{=}CMe_2 \longrightarrow CH_3{\cdot}CMe_2{\cdot}CH{:}CMe_2 \quad \text{(XX.)}$$

$$2.\ H_2\overset{\curvearrowleft}{C}{=}CPh_2 + H{\rightarrow}CH{=}CPh_2 \longrightarrow CH_3{\cdot}CPh_2{\cdot}CH{:}CPh_2 \quad \text{(XXI.)}$$

$$3.\ H_2\overset{\curvearrowleft}{C}{=}CHEt + H{\rightarrow}CH{=}CH_2 \longrightarrow CH_3{\cdot}CHEt{\cdot}CH{:}CH_2 \quad \text{(XXII.)}$$

$$4.\ H_2\overset{\curvearrowleft}{C}{=}CMe_2 + H{\rightarrow}C(CMe_3){=}CMe_2 \longrightarrow CH_3{\cdot}CMe_2{\cdot}C(CMe_3){:}CMe_2 \quad \text{(XXIII.)}$$

5.



(XXIV.)

The self-addition of mono-olefins, whether of the same or of different molecular species, appears to be jointly dependent on (*a*) the capacity of a hydrogen atom in one of the reactant molecules (the addendum) to suffer incipient ionisation in the manner $H{\rightarrow}\overset{\delta+}{C_1}{=}\overset{\delta-}{C_2}$, and (*b*) the occurrence of successful polarisation at the double bond of the other.[55] The process (*a*) is promoted by electromeric changes in the opposite (usually less-favoured) direction to those utilised in (*b*), and polymerisation can only occur to the extent that (*a*) is achieved; the addition product then retains the double bond of the addendum molecule, according to the generalised scheme :

$$\overset{\delta-}{C}HR^1\overset{\curvearrowleft}{=}\overset{\delta+}{C}R^2R^3 + \overset{\delta+}{H}{\rightarrow}\overset{\delta-}{C}R^4{=}CR^5R^6 \longrightarrow CH_2R^1{\cdot}CR^2R^3{\cdot}CR^4{=}CR^5R^6$$

The formation of addition products by the interaction of styrene and different benzene hydrocarbons in presence of sulphuric acid [56] (*e.g.*, $CHPh{:}CH_2 + C_6H_6 \longrightarrow CHPh_2{\cdot}CH_3$) appears to be an analogous process.

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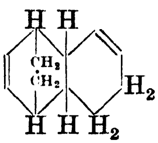
[54] E. Bergmann and H. Taubadel, *Ber.*, 1932, **65**, [*B*], 463; *A.*, 507. Compare G. S. Whitby and M. Katz, *J. Amer. Chem. Soc.*, 1928, **50**, 1160; *A.*, 1928, 627; *Canadian J. Res.*, 1931, **4**, 344; *A.*, 1931, 833.

[55] Compare *Ann. Reports*, 1930, **27**, 91, 92; 1931, **28**, 87; E. Bergmann and H. Weiss, *Annalen*, 1930, **480**, 49; *A.*, 1930, 901; E. Bergmann, H. Taubadel, and H. Weiss, *Ber.*, 1931, **64**, [*B*], 1493; *A.*, 1931, 945.

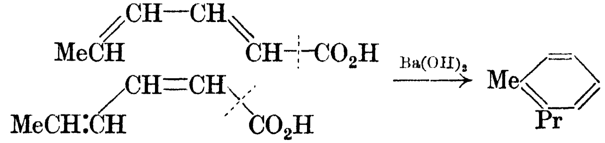
Acetylenes. Acetylene polymerises catalytically at low temperatures in the presence of ammonium and cuprous chlorides to produce a dimeride (vinylacetylene), a trimeride (divinylacetylene), and a tetrameride (probably $CH_2{:}CH{\cdot}C{:}C{\cdot}CH{:}CH{\cdot}CH{:}CH_2$). The dimeride can definitely yield the tetrameride by self-addition under the conditions of the reaction and appears to yield the trimeride by combination with acetylene.[57] Polymerisation is limited to compounds containing the group $\cdot C{:}CH$, consequently the trimeride and the tetrameride are the ultimate products of the reaction. The process is of the same general character as that occurring in the polymerisation of the mono-olefins and it is noteworthy that the reaction (*A*) proceeds in preference to (*B*):

$$(A)\ CH_2{:}CH{\cdot}C{:}C{-}H + CH{:}CH \longrightarrow CH_2{:}CH{\cdot}C{:}C{\cdot}CH{:}CH_2$$
$$(B)\ CH_2{:}CH{\cdot}C{:}CH + H{-}C{:}CH \longrightarrow CH_2{:}CH{\cdot}CH{:}CH{\cdot}C{:}CH$$

Diolefins. The characteristic mode of dimerisation of conjugated butadienoid compounds is closely related to the Diels–Alder reaction. In last year's Report reference was made to the elucidation of the manner of dimerisation of *cyclo*pentadiene: during the present year the manner of dimerisation in two other outstanding instances has been determined. The remarkably stable dimeride of *cyclo*hexadiene is constituted analogously to di*cyclo*pentadiene,[58] and the hydrocarbon derived by the combined decarboxylation and polymerisation of sorbic acid (Doebner's supposed tri*cyclo*octane) is now recognised to be *o*-propyltoluene.[59] The latter mode of reaction is reproduced in the case of cinnamenylacrylic acid and also of β-vinylacrylic acid, which yield the aromatic hydrocarbons, $o\text{-}Ph{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2Ph$ and ethylbenzene respectively.



Dicyclo-hexadiene



Doebner's hydrocarbon

All dimerisations of butadienoid hydrocarbons in which the constitution of the product has been satisfactorily established yield, so far as is known, derivatives of *cyclo*hexene. Hitherto, however, there has been little to indicate how the trimerisation and tetramerisation of butadienoid compounds proceed. The work of K. Alder and his collaborators on the trimerides of *cyclo*pentadiene [60] throws some light on the subject. Tri*cyclo*pentadiene is formed by the addition of *cyclo*pentadiene to di*cyclo*pentadiene at the double bond in the bridged *cyclo*hexene ring of the latter.

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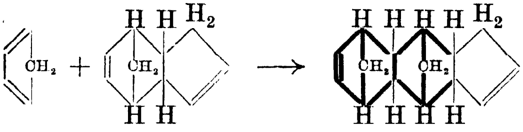
[56] A. Spilker and W. Schade, *Ber.*, 1932, **65**, [*B*], 1686.

[57] J. A. Nieuwland, W. S. Calcott, F. B. Downing, and A. S. Carter, *J. Amer. Chem. Soc.*, 1931, **53**, 4197; *A.*, 1932, 40.

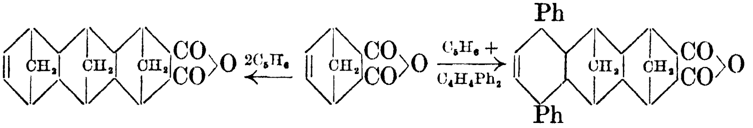
[58] K. Alder and G. Stein, *Annalen*, 1932, **496**, 197; *A.*, 938.

[59] R. Kuhn and A. Deutsch, *Ber.*, 1932, **65**, [*B*], 43; *A.*, 258.



Dicyclopentadiene *Tricyclopentadiene*

Two forms of the trimeride are obtained and since the spatial configuration of that portion of the carbon skeleton represented by thick lines in the formula has been shown to be exactly the same in each case, the isomerism is to be attributed to the alternative spatial arrangements that can be assumed by the *cyclo*pentene ring with respect to the plane of the adjoining ring. It is probable, indeed, that the two forms of the trimeride arise by addition to the two known forms of the dimeride respectively. Polymerisation can go still further to the tetrameride stage. Now since the " mixed " addition products (XXVI) and (XXVII) can be respectively obtained by the addition of successive molecules of *cyclo*pentadiene to the compound (XXV) (itself derived by the union of *cyclo*pentadiene with maleic anhydride) and by the addition of *cyclo*pentadiene and αδ-diphenylbutadiene successively to (XXV),



(XXVI.) (XXV.) (XXVII.)

there is strong indication that the more reactive double bond in any butadiene dimeride or trimeride is normally the one in the bridged *cyclo*hexene ring.

A study of the polymerisation of eleven simple butadienes under the influence of heat or of chemical agents [61] shows that dimerides (one or more in each case) are invariably formed. In some cases higher polymerides are also formed, but the presence of at least three unsubstituted hydrogen atoms on the terminal carbon atoms appears to be necessary for the formation of a synthetic rubber. The dimerides are themselves polymerised in the cold by certain inorganic reagents (H_2SO_4, $SbCl_5$, $SnCl_4$, etc.), but there is nothing as yet to show that their formation constitutes an intermediate step in the formation of normal rubbers.

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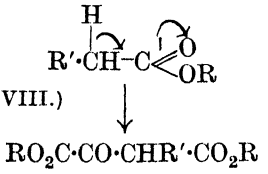
[60] K. Alder, G. Stein, and others, *Annalen*, 1932, **496**, 204; *A.*, 938.

[61] G. S. Whitby and R. N. Crozier, *Canadian J. Res.*, 1932, **6**, 203; *A.*, 361; G. S. Whitby and W. Gallay, *ibid.*, p. 280; *A.*, 496.

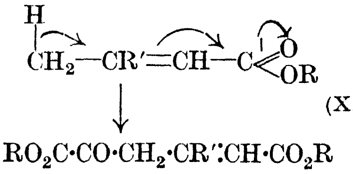
Refractivity, Condensations, and Structural Mobility.—The simple butadienoid hydrocarbons, when prepared by the best methods available, show considerable variations in boiling point, density, refractive index, and dielectric constant, although when submitted to the Diels–Alder reaction as a chemical test of homogeneity they show no signs of marked heterogeneity. These physical differences, which do not occur in examples where geometrical isomerism is impossible, are attributed to the presence of *cis-* and *trans-*forms, or in the case of αδ-dialkylbutadienes, possibly to the presence of *cis-cis, cis-trans,* and *trans-trans* forms. The optical properties of the mono- and di-methylbutadienes are also discussed, but for details the reader is referred to the original paper.[62] The optical properties of a number of aryl-polyacetylenes have also been investigated and values for the molecular exaltation due to the CPh⁚C group obtained.[63] These values vary considerably according to the solvent employed, but an average value, EM_D 3·29, is recorded.

The transmission of electrical influences through conjugated carbon systems is well seen from a number of new examples of well-known reactivities. The first of these concerns the formation of oxalyl derivatives by the action of oxalic ester on carboxylic esters or ketones in the presence of sodium or potassium ethoxide.



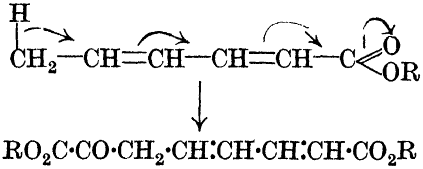
(XXVIII.)

$$\mathrm{R'{\cdot}\overset{H}{C}H{-}C{<}^{O}_{OR}} \;\downarrow\; \mathrm{RO_2C{\cdot}CO{\cdot}CHR'{\cdot}CO_2R}$$



(XXIX.)

$$\mathrm{\overset{H}{C}H_2{-}CR'{=}CH{-}C{<}^{O}_{OR}} \;\downarrow\; \mathrm{RO_2C{\cdot}CO{\cdot}CH_2{\cdot}CR'{:}CH{\cdot}CO_2R}$$



(XXX.)

$$\mathrm{\overset{H}{C}H_2{-}CH{=}CH{-}CH{=}CH{-}C{<}^{O}_{OR}} \;\downarrow\; \mathrm{RO_2C{\cdot}CO{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CO_2R}$$

The detachment of a proton from the α-methylene group of a fatty acid ester (XXVIII) at the instance of the reagent is rendered possible by the juxtaposition of the carbonyl group, so that an oxalyl group is enabled to enter the molecule at this point. The same effect obtains if an ethylenic grouping, $C\dot{:}C\cdot$, is interposed between the α-methylene group and the carbonyl group, as was discovered by A. Lapworth [64] in working with β-alkylacrylic esters (XXIX), and has now been shown to occur in the case of sorbic ester (XXX).[65]

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[62] E. H. Farmer and F. L. Warren, *J.*, 1931, 3221; *A.*, 1932, 141.

[63] V. Krestinski and N. Perssianzeva, *Ber.*, 1931, **64,** [*B*], 2363; *A.*, 1931, 1412

The formation of aldols or their dehydration products by the interaction of unsaturated aldehydes is an analogous reactivity, and from the recently synthesised β-methylcrotonaldehyde [66] (2 mols.) the aldol $CMe_2\dot{:}CH\cdot CH(OH)\cdot CH_2\cdot CMe\dot{:}CH\cdot CHO$ and the corresponding triene-aldehyde,

$$CMe_2\dot{:}CH\cdot CH\dot{:}CH\cdot CMe\dot{:}CH\cdot CHO,$$

can be successively obtained.[67] Likewise, benzaldehyde and crotonaldehyde together give rise to phenylpentadienal,

$$CHPh\dot{:}CH\cdot CH\dot{:}CH\cdot CHO,^{68}$$

whilst crotonaldehyde (2 mols.) yields an unbranched aldol, doubtless $CHMe\dot{:}CH\cdot CH(OH)\cdot CH_2\cdot CH\dot{:}CH\cdot CHO$.[69] Acetaldehyde and crotonaldehyde, when condensed together, give hexadienal, $CH_3\cdot[CH\dot{:}CH]_2\cdot CHO$, which yields with more acetaldehyde, octatrienal, $CH_3\cdot[CH\dot{:}CH]_3\cdot CHO$.[70] The same type of reactivity does not, however, extend to the condensation of aldehydes with unsaturated acids. Thus under the conditions of the Perkin reaction no condensation occurs between benzaldehyde, potassium crotonate, and crotonic anhydride, but in the presence of *tert.*-bases, benzaldehyde and crotonic anhydride react to give, not δ-phenyl-$\Delta^{\alpha\gamma}$-pentadienoic acid, but α-vinylcinnamic acid,

$$CHPh\dot{:}C(CO_2H)\cdot CH\dot{:}CH_2.^{71}$$

Probably here the mixed enolic anhydride,

$$CHMe\dot{:}CH\cdot CO\cdot O\cdot C(OH)\dot{:}CH\cdot CH\dot{:}CH_2,$$

is formed intermediately.

A peculiar type of aldehyde condensation which appears to proceed in the manner of the Diels–Alder reaction is afforded by the self-condensation of β-methylcrotonaldehyde in the presence of sodamide. The aldehyde in this case gives rise to the cyclic aldehyde (XXXI), and citral, with the same condensing agent, gives

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[64] *J.*, 1901, **79**, 1276; see also L. Higginbotham and A. Lapworth, *J.*, 1923, **123**, 1325.

[65] W. Borsche and R. Manteuffel, *Ber.*, 1932, **65**, [*B*], 868; *A.*, 721.

[66] F. G. Fischer, L. Ertel, and K. Löwenberg, *ibid.*, 1931, **64**, [*B*], 30; *A.*, 1931, 335.

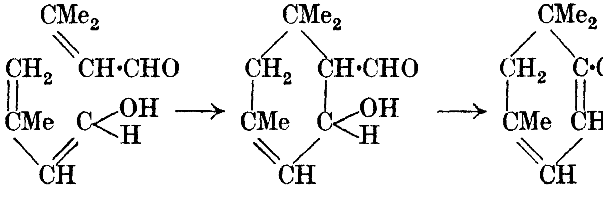
[67] F. G. Fischer and K. Löwenberg, *Annalen*, 1932, **494**, 263; *A.*, 600; compare K. Bernhauer and E. Woldan, *Biochem. Z.*, 1932, **249**, 199; *A.*, 834.

[68] R. Kuhn and A. Winterstein, *Helv. Chim. Acta*, 1929, **12**, 493; *A.*, 1929, 699.

[69] (Miss) I. Smedley, *J.*, 1911, **99**, 1627.

[70] R. Kuhn and M. Hoffer, *Ber.*, 1930, **63**, [*B*], 2163; 1931, **64**, [*B*], 1977; *A.*, 1930, 1406; 1931, 1273.

[71] R. Kuhn and S. Ishikawa, *ibid.*, p. 2347; *A.*, 1931, 1413.

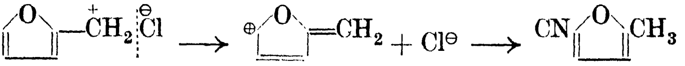

(XXXI.)

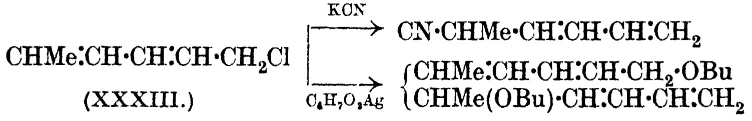
an exactly analogous product; crotonaldehyde, on the other hand, gives a resin.[67]

Isomeric Change.—Anionotropic changes closely resembling that which occurs during the isomerisation of the αβ-dibromide of hexatriene

$$(CH_2Br{\cdot}\overset{\oplus}{C}H{\cdot}CH{:}CH{\cdot}CH{:}CH_2 + \overset{\ominus}{Br} \longrightarrow CH_2Br{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH_2Br)$$

have been observed to occur when furfuryl chloride (XXXII) and sorbyl chloride (XXXIII) react with potassium cyanide.[72] In


(XXXII.)



$$CHMe{:}CH{\cdot}CH{:}CH{\cdot}CH_2Cl \begin{cases} \xrightarrow{KCN} CN{\cdot}CHMe{\cdot}CH{:}CH{\cdot}CH{:}CH_2 \\ \xrightarrow[C_4H_7O_2Ag]{} \begin{cases} CHMe{:}CH{\cdot}CH{:}CH{\cdot}CH_2{\cdot}OBu \\ CHMe(OBu){\cdot}CH{:}CH{\cdot}CH{:}CH_2 \end{cases} \end{cases}$$

(XXXIII.)

these cases the transference of the cyanide radical to the remote end of the conjugated system appears to reach completion, but in the instance of the cyanide derived from 5-methylfurfuryl chloride and in that of the butoxy-compound derived from sorbyl chloride by the action of silver butyrate a mixture of isomeric compounds is obtained.

Synthesis of Ethylenic Nitriles.—Much new information is now available concerning the methods of synthesis of *cis*- and *trans*-forms of Δ^{α}- and Δ^{β}-ethylenic nitriles, including compounds of the penteno-,[73] hexeno-,[74] *iso*hexeno-,[75] hepteno-,[76] and *iso*hepteno-[77] series.

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[72] T. Reichstein, *Ber.*, 1930, **63**, [*B*], 749; *A.*, 1930, 611; T. Reichstein and H. Zschokke, *Helv. Chim. Acta*, 1932, **15**, 249; *A.*, 519; T. Reichstein and G. Trivelli, *ibid.*, p. 254; *A.*, 498.

Trienes and Tetraenes.

The isolation by R. S. Cahn, A. R. Penfold, and J. L. Simonsen [78] of an open-chain triene-carboxylic acid from the wood-oil of *Callitropsis araucarioides* has directed attention to the synthesis of conjugated triene acids. The acid of Simonsen and his collaborators, which contained one double bond more than geranic acid, absorbed three mols. of hydrogen on catalytic hydrogenation to give the already-known *dl*-tetrahydrogeranic acid. It was therefore a dehydrogeranic acid containing the carbon skeleton of geranic acid, and therefore one of seven triene isomerides possessing the necessary skeleton and differing from one another only in the position of the double bonds. The most probable formula for the acid was the fully-conjugated one, $CMe_2\!:\!CH{\cdot}CH\!:\!CH{\cdot}CMe\!:\!CH{\cdot}CO_2H$, in spite of the fact that no addition product with maleic anhydride had been obtainable.

Now the introduction of a methyl group into the β-position during the synthesis of a conjugated acid can usually be achieved by submitting such a ketone as mesityl oxide to the Reformatsky reaction; but here the ketone requisite for the production of a terminal *iso*propylidene group in a conjugated chain was that homologue of the well-known crotylideneacetone which should be capable of synthesis from F. G. Fischer, L. Ertel, and K. Löwenberg's β-methylcrotonaldehyde. The successful synthesis of this ketone,

$$CMe_2\!:\!CH{\cdot}CH\!:\!CH{\cdot}CO{\cdot}CH_3,$$

by Fischer and Löwenberg was followed by its submission to the Reformatsky reaction with bromoacetic ester. Thus was obtained a hydroxy-ester, $CMe_2\!:\!CH{\cdot}CH\!:\!CH{\cdot}CMe(OH){\cdot}CH_2{\cdot}CO_2Me$, from which by dehydration and hydrolysis a solid dehydrogeranic acid identical with Cahn, Penfold, and Simonsen's acid was derived.[79] This acid was accompanied by an oily acid which apparently represented or contained a geometrical isomeride of the first, since it gave dimethylheptatriene on decarboxylation.

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[73] P. Bruylants and G. Jmoudsky, *Bull. Acad. roy. Belg.*, 1931, [v], **17**, 1161; *A.*, 1932, 257.

[74] P. Bruylants and L. Ernould, *ibid.*, p. 1174; *A.*, 1932, 258; R. A. Letch and R. P. Linstead, *J.*, 1932, 443; *A.*, 371; P. Bruylants, *Bull. Soc. chim. Belg.*, 1932, **41**, 309; *A.*, 1119; A. Dewael, *ibid.*, p. 318; *A.*, 1119.

[75] J. Baerts, *ibid.*, p. 314; *A.*, 1119; P. Bruylants, *Bull. Acad. roy. Belg.*, 1931, [v], **17**, 1008; *A.*, 1931, 1403; P. Bruylants and L. Ernould, *ibid.*, p. 1027; *A.*, 1931, 1403.

[76] P. Bruylants, *Bull. Soc. chim. Belg.*, 1932, **41**, 333; *A.*, 1119.

[77] G. Festraete, *ibid.*, p. 327; *A.*, 1119.

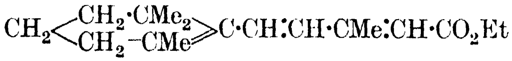
[78] *J.*, 1931, 3134; *A.*, 1932, 144.

[79] *Annalen*, 1932, **494**, 263; *A.*, 600.

The same synthesis was effected independently by R. Kuhn and M. Hoffer,[80] likewise employing the diene ketone derived from β-methylcrotonaldehyde. Here, however, the Reformatsky product yielded, when dehydration was effected before hydrolysis, a mixture of Cahn, Penfold, and Simonsen's acid (m. p. 186°) and a solid isomeride (m. p. 137°) thereof; but when hydrolysis and dehydration were effected in one operation, only the lower-melting isomeride was obtained. The two acids show almost identical absorption spectra and doubtless differ in the geometrical configuration about the αβ-double bond. Kuhn and his collaborators draw attention to the approximately constant difference in melting point between all such pairs of *trans*- and *cis*-isomerides belonging to the mono-olefin, diene, and triene series of monocarboxylic acids respectively.

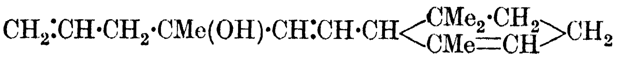
Triene acids analogous to the above but containing the ring of ionone have also been derived by submitting β-ionone to the Reformatsky reaction with bromoacetic ester and hydrolysing the triene ester (XXXIV) thereby immediately obtained.[81] The acids (solid and liquid) in this case also were probably geometrical isomerides.

(XXXIV.)



$$CH_2{<}\begin{matrix}CH_2\cdot CMe_2\\ CH_2-CMe\end{matrix}{>}C\cdot CH{:}CH\cdot CMe{:}CH\cdot CO_2Et$$

(XXXV.)



$$CH_2{:}CH\cdot CH_2\cdot CMe(OH)\cdot CH{:}CH\cdot CH{<}\begin{matrix}CMe_2\cdot CH_2\\ CMe{=}CH\end{matrix}{>}CH_2$$

A related synthesis has been effected by treating α-ionone with allylmagnesium bromide, the product being the hydroxy-hydrocarbon (XXXV), from which the corresponding trimethyl*cyclo*hexenylmethylhexatriene is obtained on dehydration.

The alcohols corresponding to Kuhn and Hoffer's *n*-octatrienal and *n*-decatetraenal have been obtained by reducing the aldehydes with aluminium *iso*propoxide. Both *n*-octatrienol,

$$\begin{matrix}CH_3\cdot CH{:}CH\cdot CH{:}CH,\\ HO\cdot CH_2\cdot CH{:}CH\end{matrix}$$

and *n*-decatetraenol,

$$\begin{matrix}CH_3\cdot CH{:}CH\cdot CH{:}CH,\\ HO\cdot CH_2\cdot CH{:}CH\cdot CH{:}CH\end{matrix}$$

like sorbyl alcohol, are crystalline solids unstable in air.[82]

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[80] *Ber.*, 1932, **65**, [*B*], 651; *A.*, 600; see also R. Kuhn and H. Roth, *ibid.*, p. 1285; *A.*, 1111.

[81] P. Karrer, H. Salomon, R. Morf, and O. Walker, *Helv. Chim. Acta*, 1932, **15**, 878; *A.*, 852.

[82] T. Reichstein, C. Ammann, G. Trivelli, and others, *ibid.*, p. 261; *A.*, 496.

Several interesting considerations arise out of the observed behaviour of polyene-carboxylic acids on reduction. As was shown by J. T. Evans and E. H. Farmer,[83] the reductive behaviour of sorbic acid when treated by metals in aqueous media varies with the acidity or alkalinity of the medium, but both αβ- and αδ-dihydrogenated (Δ^{γ}- and Δ^{β}-dihydro-)products are always formed. A similar production of isomeric dihydro-acids by αβ- and terminal addition (possibly also by αδ-, etc., addition in the case of trienes and higher polyenes) is generally to be expected with all conjugated polyene-monocarboxylic acids, although theoretical considerations indicate that the proportions must vary with the character of the substitution in the polyene chain and in some cases one of the forms may be absent, or present in but small amount, or may even be so unstable as to suffer double-bond migration immediately after production. Although in the sorbic acid series dual modes of reduction have been shown to apply generally,[84] experiments by R. Kuhn and A. Winterstein on the reduction of αω-diphenylpolyenes have given only terminally additive products;[85] also from the (monomeric) reduction products of the triene- and tetraene-acids, $CH_3{\cdot}[CH{:}CH]_3{\cdot}CO_2H$ and $CH_3{\cdot}[CH{:}CH]_4{\cdot}CO_2H$, only terminal addition products have as yet been isolated.[86] A noteworthy point here, however, is that the $\Delta^{\beta\delta}$-dihydro-derivative of the triene acid suffers transference of the conjugated system (as a whole) towards the carboxyl group when heated with alkali under the usual conditions of the βγ,αβ-change:

$$CH_3{\cdot}CH_2{\cdot}[CH{:}CH]_2{\cdot}CH_2{\cdot}CO_2H \longrightarrow CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}[CH{:}CH]_2{\cdot}CO_2H$$

In these reductions, as in those of the αω-diphenylpolyenes and indeed of all other reductions of polyene systems so far described, there has been no indication of the production of geometrically isomeric polyene-reduction products. In all terminal additions the distinction between *cis*- and *trans*-forms appears to be obliterated during the reaction, for reasons which are quite intelligible having regard either to electronic or to classical representations of the valency changes which occur in the processes;[87] moreover, so far as present evidence shows, the resulting configurations about the individual double bonds are all of *trans*-character.[88]

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[83] *J. Soc. Chem. Ind.*, 1928, **47**, 268; *J.*, 1928, 1644; *A.*, 1928, 868.

[84] *Ann. Reports*, 1930, **27**, 87.

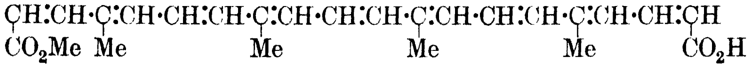
[85] *Helv. Chim. Acta*, 1928, **11**, 123; *A.*, 1928, 281.

[86] R. Kuhn and M. Hoffer, *Ber.*, 1932, **65**, [*B*], 170; *A.*, 365.

[87] Compare E. H. Farmer and W. M. Duffin, *J.*, 1927, 405; *A.*, 1927, 448; E. H. Farmer, B. D. Laroia, T. M. Switz, and J. F. Thorpe, *ibid.*, p. 2937; *A.*, 1928, 151; E. H. Farmer and F. L. Warren, *J.*, 1929, 897, 901; *A.*, 1929, 812.

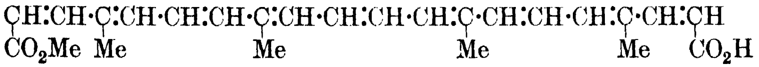
Polyenes.

Bixin and Crocetin.—The foregoing consideration respecting the geometrical form of reduction products is of importance in connexion with the inter-relationship of bixin and β-bixin, the latter of which can be converted into the former by the addition and removal of iodine. The probability that the two substances are *cis-trans* isomerides seemed somewhat diminished by the fact that the formation of *iso*carotin from β-carotin, which likewise occurs by the action of iodine, involves no *cis-trans* rearrangement: but in the latter case strictly stoicheiometrical proportions of iodine are found to be necessary for the conversion, whereas in the former only a trace of iodine is required. The two bixins give on reduction dihydro-compounds which are identical and of which the methyl esters are identical: hence it appears that they are geometrical isomerides, but there is no indication as to whether *only* one, or more than one, *cis*-unit is present in the molecule of bixin (α-).[89]



$$\underset{\mathrm{CO_2Me}}{\mathrm{CH}}\mathrm{{:}CH{\cdot}}\underset{\mathrm{Me}}{\mathrm{C}}\mathrm{{:}CH{\cdot}CH{:}CH{\cdot}}\underset{\mathrm{Me}}{\mathrm{C}}\mathrm{{:}CH{\cdot}CH{:}CH{\cdot}}\underset{\mathrm{Me}}{\mathrm{C}}\mathrm{{:}CH{\cdot}CH{:}CH{\cdot}}\underset{\mathrm{Me}}{\mathrm{C}}\mathrm{{:}CH{\cdot}CH{:}}\underset{\mathrm{CO_2H}}{\mathrm{CH}}$$

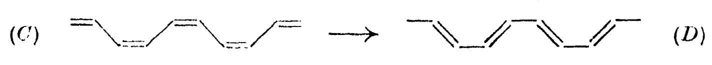
Bixin (Kuhn and Winterstein, 1928) (XXXVI.)



$$\underset{\mathrm{CO_2Me}}{\mathrm{CH}}\mathrm{{:}CH{\cdot}}\underset{\mathrm{Me}}{\mathrm{C}}\mathrm{{:}CH{\cdot}CH{:}CH{\cdot}}\underset{\mathrm{Me}}{\mathrm{C}}\mathrm{{:}CH{\cdot}CH{:}CH{\cdot}CH{:}}\underset{\mathrm{Me}}{\mathrm{C}}\mathrm{{\cdot}CH{:}CH{\cdot}CH{:}}\underset{\mathrm{Me}}{\mathrm{C}}\mathrm{{\cdot}CH{:}}\underset{\mathrm{CO_2H}}{\mathrm{CH}}$$

Bixin (symmetrical formulation) (XXXVII.)

Analysis of the absorption spectra of the various compounds strongly indicates that dihydrobixin arises by the terminal addition of hydrogen to the parent compounds, and in such a process geometrical considerations indicate that homogeneous *trans, trans*.....- and *cis, cis*.....-systems (*A* and *C* respectively) can alike pass into homogeneous *trans, trans*.....-chains.



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[88] The case of ββ′-diphenylmuconic acid, however, appears at present to afford an exception (Farmer and Duffin, *loc. cit.*). One of the two known geometrically isomeric forms of this acid yields the *cis*-dihydro-acid on reduction with sodium amalgam, and the other a mixture of *cis*- and *trans*-dihydro-acids. This result may mean that the addition (owing to the influence of the phenyl groups) does not take place terminally, or that certain types of substitution can exert a determining influence on configuration during the passage from the intermediate (non-double bonded) stage of reduction to the final stage at which reduced products of definite geometrical form appear.

If *trans*-linkings usually occurred in the form (*D*) [obtainable from (*A*) by rotation about the single bonds], the appearance of *cis*-linkings in the building up of dihydro-polyenes might be geometrically conceivable; but such configurations in conjugated compounds—at least in the crystalline condition—have not yet been observed and the *X*-ray analysis of *trans*, *trans*....-polyenes agrees better with the form (*A*).[89] At present there is no reason to assume, as has formerly been done for glutaconic acid and muconic acid, that in long-chain polyenes all distinctions between *cis*- and *trans*-configurations about the individual double bonds disappear, and the revival by D. Rădulescu[90] of electronic formulæ (other than as reaction formulæ) in which distinctions between *cis*- and *trans*-configurations disappear[91] has no experimental justification or demonstrated probability—although the synthesis, for instance, of the 72 geometrical isomerides of 1 : 14-diphenyltetradecaheptaene seems a somewhat remote event.

The reported non-equivalence of the carboxyl groups in bixin may be due therefore to a single *cis*-linking placed unsymmetrically in the chain, and the four methyl substituents, the positions of which have not yet been determined, may well occupy symmetrical positions in the chain as in (XXXVII),[89] rather than as in (XXXVI). According to (XXXVII) bixin would represent the middle fragment of the lycopene molecule as formulated by P. Karrer and his collaborators[92] and it is possible that bixin is derived from lycopene, or a polyene closely related thereto, by oxidative degradation.

A remarkable feature of dihydromethylbixin and of the dimethyl ester of crocetin is that these substances are smoothly dehydrogenated to β-methylbixin and to the dimethyl ester of crocetin respectively by secondary and tertiary amines in the presence of air;[93] both substances, moreover, yield vivid colour reactions when treated with caustic alkali in pyridine, the coloured solutions (emerald-green and indigo-blue respectively) yielding the dehydrogenated products when shaken with oxygen. This behaviour is related to the capacity of glutaconic ester, Δ^{β}-dihydromuconic ester, and other allied substances to give deep yellow or red sodio-derivatives with alcoholic sodium ethoxide, or with caustic soda–

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[89] R. Kuhn and A. Winterstein, *Ber.*, 1932, **65**, [*B*], 646; *A.*, 618.

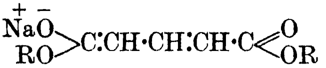
[90] *Ber.*, 1931, **64**, [*B*], 2223; *A.*, 1931, 1351.

[91] Compare G. Wittig and W. Wiemer, *Annalen*, 1930, **483**, 144; *A.*, 1931, 92.

[92] *Helv. Chim. Acta*, 1930, **13**, 1084; *A.*, 1930, 1422.

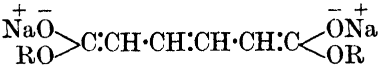
[93] R. Kuhn and P. J. Drumm, *Ber.*, 1932, **65**, [*B*], 1458; *A.*, 1138.

pyridine (aq.), and is doubtless due to the formation of enolic sodio-derivatives in the groups $\cdot CH{:}CH\cdot CH_2\cdot CO_2R$.



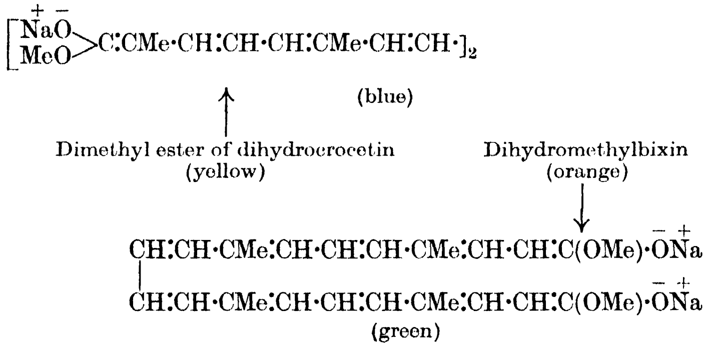
$$\begin{matrix}\overset{+}{\mathrm{Na}}\overset{-}{\mathrm{O}}\\ \mathrm{RO}\end{matrix}\!>\mathrm{C{:}CH{\cdot}CH{:}CH{\cdot}C}\!<\!\begin{matrix}\mathrm{O}\\ \mathrm{OR}\end{matrix}$$

Sodio-glutaconic ester (yellow)



$$\begin{matrix}\overset{+}{\mathrm{Na}}\overset{-}{\mathrm{O}}\\ \mathrm{RO}\end{matrix}\!>\mathrm{C{:}CH{\cdot}CH{:}CH{\cdot}CH{:}C}\!<\!\begin{matrix}\overset{-}{\mathrm{O}}\overset{+}{\mathrm{Na}}\\ \mathrm{OR}\end{matrix}$$

Sodio-dihydromuconic ester (red)



$$\left[\begin{matrix}\overset{+}{\mathrm{Na}}\overset{-}{\mathrm{O}}\\ \mathrm{MeO}\end{matrix}\!>\mathrm{C{:}CMe{\cdot}CH{:}CH{\cdot}CH{:}CMe{\cdot}CH{:}CH{\cdot}}\right]_2$$

$$\begin{matrix}\mathrm{CH{:}CH{\cdot}CMe{:}CH{\cdot}CH{:}CH{\cdot}CMe{:}CH{\cdot}CH{:}C(OMe){\cdot}\overset{-}{O}\overset{+}{Na}}\\ |\\ \mathrm{CH{:}CH{\cdot}CMe{:}CH{\cdot}CH{:}CH{\cdot}CMe{:}CH{\cdot}CH{:}C(OMe){\cdot}\overset{-}{O}\overset{+}{Na}}\end{matrix}$$

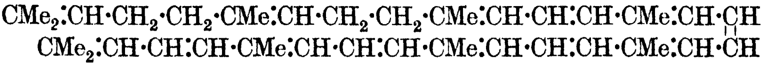
The auto-oxidation of dihydromethylbixin in the presence of caustic soda results rapidly in the removal of the two hydrogen atoms from the α-carbon atoms according to the equation :

$$C_{26}H_{34}O_4 + O_2 \longrightarrow C_{26}H_{32}O_4 + H_2O_2.^{94}$$

Lycopene and β-*Carotene.*—Lycopene, $C_{40}H_{56}$, yields on gentle oxidation with chromic acid a C_8-ketone, $CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot COMe$, the balance of the molecule being represented by a new aldehyde, lycopenal, $C_{32}H_{42}O$, which contains an *iso*propylidene group and ten double bonds in the carbon chain.[95] Spectroscopic examination of the aldehyde and its oxime indicates that the aldehyde group is probably conjugated with the double bonds of the chain as required by the formula (XXXVIII) suggested by P. Karrer and his collaborators,[96] but the evidence here is not decisive and does not exclude the possibility that lycopenal possesses a structure corresponding to the lycopene formula (XXXIX), which, like (XXXVIII), fits the facts so far known about the lycopene constitution.

$$[CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CMe{:}CH\cdot CH{:}CH\cdot CMe{:}CH\cdot CH{:}CH\cdot CMe{:}CH\cdot CH{:}]_2$$

(XXXVIII.)



$$\begin{matrix}\mathrm{CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH{:}CH{\cdot}CMe{:}CH{\cdot}CH}\\ \mathrm{CMe_2{:}CH{\cdot}CH{:}CH{\cdot}CMe{:}CH{\cdot}CH{:}CH{\cdot}CMe{:}CH{\cdot}CH{:}CH{\cdot}CMe{:}CH{\cdot}CH}\end{matrix}$$

(XXXIX.)

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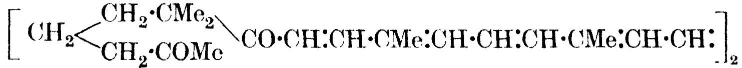
[94] R. Kuhn, P. J. Drumm, M. Hoffer, and E. F. Möller, *Ber.*, 1932, **65**, [*B*], 1785.

[95] R. Kuhn and C. Grundmann, *ibid.*, p. 898; *A.*, 749.

[96] *Helv. Chim. Acta*, 1930, **13**, 1084; 1931, **14**, 435; *A.*, 1930, 1422; 1931, 597.

It has been shown that β-carotene suffers oxidation on careful treatment with chromic acid to yield a β-oxycarotene which appears to have the empirical formula $C_{40}H_{58}O_3$, containing without doubt one β-ionone ring undamaged—a feature which results in the preservation of the growth-promoting effect characteristic of β-carotene. With a larger amount of chromic acid a second oxidation product, apparently $C_{40}H_{56}O_4$, is obtained which does not appear to be derived by way of β-oxycarotene. This substance, to which the name of β-carotenone has been given, appears to be derived by the specific oxidation of the double bonds of the β-ionone rings in β-carotene as shown in formula (XL).[97]

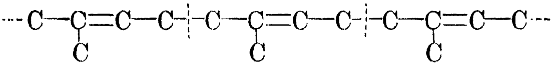


$$\left[CH_2{<}\begin{matrix}CH_2\cdot CMe_2\diagdown\\ CH_2\cdot COMe\end{matrix}CO\cdot CH{:}CH\cdot CMe{:}CH\cdot CH{:}CH\cdot CMe{:}CH\cdot CH{:}\right]_2$$

(XL.)

Rubber.

Natural Rubber.—A series of investigations on the structure of natural rubber has been carried out by T. Midgley, jun., and A. L. Henne.[98] When crêpe rubber is rapidly distilled, the distillate obtained, although consisting largely of isoprene, dipentene, and heveen (C_{15}-hydrocarbon), contains a number of other hydrocarbons in smaller or greater quantity. All of the recognisable products, containing from five to ten carbon atoms in the molecule, were found to possess structures which could have been derived from the rubber unit, $-C-\underset{C}{C}=C-C-$ or $-C-\underset{C}{\overset{|}{C}}-\overset{|}{C}-C-$, by simple operations (hydrogenation, dehydrogenation, double-bond migration, self-addition). From the proportions of the various products obtained, it appears that there is little tendency for the carbon skeleton of the rubber molecule, as represented in the Pickles formula,



$$\cdots C-\underset{C}{C}=C-C\,\vdots\,-C-\underset{C}{C}=C-C-\vdots-C-\underset{C}{C}=C-C\cdots$$

to suffer fission at points other than those single bonds which are farthest removed from the double bonds.

As the result of a study of the precipitation of rubber from an alcohol–benzene medium it is claimed that individual long-chain components of rubber can be characterised by the temperature at which precipitation occurs in a slowly cooled solution of standard composition. By means of this technique rubber is found to consist to the extent of over 50% of a single component; this is accompanied by more soluble but less definitely characterised components. Milled rubber, on the other hand, is found to be made up of a continuous series of undefined components without a single predominating individual.

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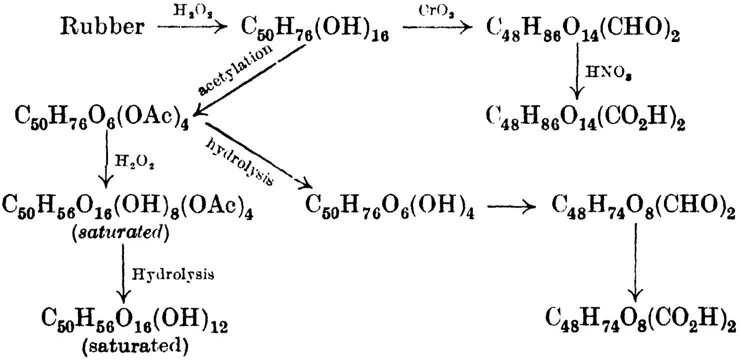
[97] R. Kuhn and H. Brockmann, *Ber.*, 1932, **65**, [*B*], 894; *A.*, 749.

[98] *J. Amer. Chem. Soc.*, 1929, **51**, 1215; *A.*, 1929, 702; *ibid.*, 1931, **53**, 203; *A.*, 1931, 357; (with M. W. Renoll) *ibid.*, p. 2733; *B.*, 1931, 853; *ibid.*, 1932 **54**, 3343, 3381; *A.*, 1036.

An interesting contribution to rubber chemistry is afforded by a new investigation of the action of hydrogen peroxide on solutions of rubber in chloroform–acetic acid.[99] Extensive oxidative hydroxylation takes place at the double bonds of the rubber molecule, but some of the double bonds appear to survive, since the product is still unsaturated, and, after acetylation, further hydroxylation can be brought about with hydrogen peroxide. During acetylation, however, some of the hydroxyl pairs appear to lose water to yield oxide rings, and some of the methylene groups of the rubber unit to suffer replacement of hydrogen by oxygen. For details of the transformations, which include the production of two dibasic acids, reference must be made to the original paper, but the main changes are shown in the following scheme, in which the primary hydroxylation product is represented on a C_{50} basis, this being the smallest molecular magnitude compatible with the analytical results obtained.



Similar operations have been carried out with gutta-percha and balata.

Artificial Rubber.—Owing to the fact that chloroprene (β-chlorobutadiene), which can readily be prepared from acetylene in a state of purity and in large quantity, polymerises about 700 times as rapidly as isoprene, it can be used as a starting material for the production of synthetic rubber.[1] Within ten days, under ordinary conditions, chloroprene polymerises into a transparent resilient mass resembling vulcanised rubber; but if polymerisation is interrupted before it has proceeded to completion, a soft plastic product (α-polymeride) resembling unvulcanised rubber is obtained. Under the action of heat the α-polymeride changes rapidly into the μ-polymeride, and by other means volatile (β)-, granular (ω-), and balata-like polymerides can be formed. The conversion of chloroprene into μ-polychloroprene is stated to proceed rapidly in aqueous emulsion, yielding a synthetic (vulcanised) latex of smaller particle size than natural latex.

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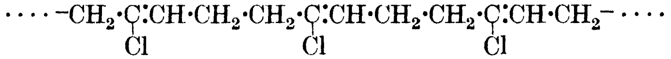
[99] J. A. Mair and J. Todd, *J.*, 1932, 386.

[1] W. H. Carothers, I. Williams, A. M. Collins, and J. E. Kirby, *J. Amer. Chem. Soc.*, 1931, **53**, 4203.

With regard to the constitution of polymerised chloroprene it appears probable that the μ-polymeride is the analogue of natural rubber and should be represented by a formula strictly analogous to that of Pickles,



$$\cdots\cdots\text{-}CH_2\cdot\underset{Cl}{C}{:}CH\cdot CH_2\cdot CH_2\cdot\underset{Cl}{C}{:}CH\cdot CH_2\cdot CH_2\cdot\underset{Cl}{C}{:}CH\cdot CH_2\text{-}\cdots\cdots$$

In conformity with this formula it is extremely resistant to alkalis (as also to hydrochloric acid, hydrofluoric acid, and many other reagents), is less reactive than natural rubber towards ozone, and yields succinic acid on oxidation. But these observations do not reveal whether a uniform attachment of chloroprene units in the manner 1 : 4—1 : 4—, etc., obtains, or whether inverted unions of the type 1 : 4—4 : 1 or 4 : 1—1 : 4— occur in the chain. Such inversions probably do not occur to any considerable extent in synthetic isoprene rubber, since the behaviour of the latter to ozone is normal,[2] and here also the *X*-ray pattern indicates that there is greater freedom from irregularities than in other synthetic rubbers.

Of other known $\Delta^{\alpha\gamma}$-chlorobutadienes, γ-chloro-β-methylbutadiene is the only one likely to serve as a precursor of rubber. In this case polymerisation occurs as rapidly as with chloroprene and the product is vulcanised by heat alone.[3] When a second methyl group is introduced into the chloroprene molecule, as in γ-chloro-$\alpha\beta$-dimethylbutadiene, the ease of polymerisation is greatly reduced, but is still superior to that of isoprene.

The nature of the product obtained by the pyrolysis of sodium rubber (polymerised isoprene), in comparison with those obtained from natural rubber, is held to indicate that the position of the methyl groups and the character of the unsaturation in methyl rubber both differ from those in natural rubber.[4] The products from sodium rubber are on the whole more saturated, showing a decrease

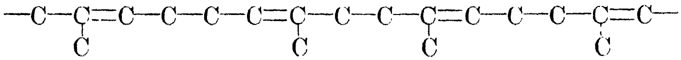
[2] Compare R. Pummerer and A. Koch, Memmler's "Handbuch der Kautschukwissenschaft," 1930, p. 270.

[3] W. H. Carothers and D. D. Coffman, *J. Amer. Chem. Soc.*, 1932, **54**, 4071; *A.*, 1232.

[4] T. Midgley, jun., A. L. Henne, and A. F. Shepard, *ibid.*, p. 381; *A.*, 276.

in the amount of isoprene and dipentene and an increase in the amount of pentenes and of saturated hydrocarbons present (saturated hydrocarbons are absent from the natural rubber distillate).

The pyrolysis results for sodium rubber agree with the arrangement of carbon atoms, but are incompatible with the regular recurrence of double bonds shown in the carbon skeleton :

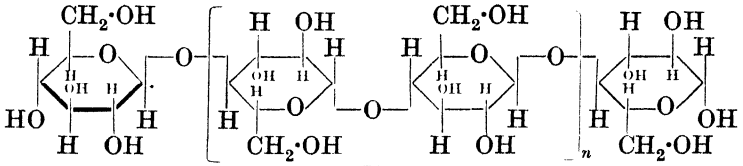


$$-\mathrm{C}-\underset{\mathrm{C}}{\mathrm{C}}=\mathrm{C}-\mathrm{C}-\mathrm{C}-\mathrm{C}=\underset{\mathrm{C}}{\mathrm{C}}-\mathrm{C}-\mathrm{C}-\underset{\mathrm{C}}{\mathrm{C}}=\mathrm{C}-\mathrm{C}-\mathrm{C}-\underset{\mathrm{C}}{\mathrm{C}}=\mathrm{C}-$$

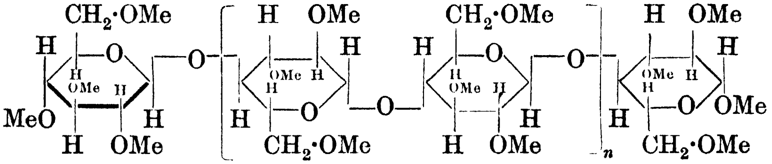
Titration of sodium rubber with bromine indicates the presence of one double bond per C_5H_8 unit, and the ozonide of sodium rubber corresponds in composition with $[C_5H_8O_3]_n$. The ozonide does not, however, break down into simple products on heating with water and it is concluded that the sodium rubber molecule is a modification, possibly cyclised, of that shown above, the modification resulting in the presence of one chemically weak bond per C_5H_8 unit.

Polysaccharides.

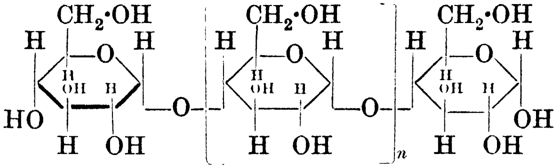
Length of Chain and Molecular Weight.—Since the cryoscopic method of determining the molecular weight of polysaccharides has in many cases proved to be unreliable, considerable interest attaches to the results afforded by purely chemical methods of estimation. A theoretically simple way of determining the length of chain of those complex open-chain substances which are built up of recurrent units consists in determining the percentage degree of occurrence of the terminal units (one or both), since these will usually permit of differentiation from the intermediate units of the chain. The method will apply whether the complex substances in question arise by the additive polymerisation of olefinic units (polystyrenes, rubber, etc.) or by the condensation-polymerisation of hydroxylated molecules (polysaccharides), so long as the ends of the chain are not joined. The practicability of the method, however, depends entirely on the reactive capacities of the terminal units whilst still forming part of the chain, on the facility with which one or other of the terminal units (or characteristic fragments thereof) can be segregated by quantitative scission of the chain, or on both properties. Thus if cellulose be represented, according to the conception which has gained almost general acceptance, as built up by the union of glucosidically-linked β-glucose units (XLI), one of the terminal units will differ from the other and from the intermediate members of the chain in the number of non-glucosidyl hydroxyl groups capable of methylation (XLII). In the same way, if starch and glycogen be represented as built up of α-glucose units (XLIII and XLIV), and inulin of fructofuranose units (XLV), the terminal C_6-units will in every case be capable of differentiation from the intermediate units, and from one another.



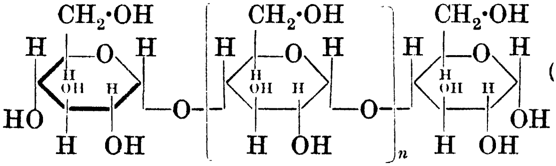
(XLI.)



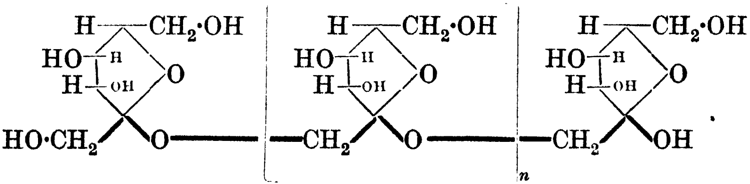
(XLII.)



(XLIII.)



(XLIV.)



(XLV.)

The method was found to be applicable equally to cellulose,[5] starch (both amylose and amylopectin portions),[6] glycogen,[7] and inulin.[8] In the first three polysaccharides the non-reducing

[5] W. N. Haworth and H. Machemer, *J.*, 1932, 2270; *A.*, 1022.

[6] E. L. Hirst, (Miss) M. M. T. Plant, and (Miss) M. D. Wilkinson, *ibid.*, p. 2375; *A.*, 1116.

[7] W. N. Haworth and E. G. V. Percival, *ibid.*, p. 2277; *A.*, 1022; see also G. K. Hughes, A. K. Macbeth, and F. L. Winzor, *ibid.*, p. 2026; *A.*, 934.

[8] W. N. Haworth, E. L. Hirst, and E. G. V. Percival, *ibid.*, p. 2384; *A.*, 1117.

terminal unit in each case was estimated after cleavage of the methylated chain and glucosidation of the fragments as tetramethyl methylglucoside, and in the case of inulin as tetramethyl methylfructoside. The length of the chain and the corresponding molecular weights so determined are shown in the table.

	No. of C_6-units.	*Mol. wt.*
Cellulose	100—200	20,000—40,000
Starch (amylose)	about 24	5,000
„ (amylopectin)	„	„
Glycogen	about 12	2,500
Inulin	30	5,000

The value to be attached to these figures depends of course on the extent to which scission of the original polysaccharide chains has been avoided in the preparation of the fully methylated product and this consideration is of the utmost importance with a polysaccharide so susceptible of degradation as inulin. The production of fully methylated polysaccharides, under conditions precluding degradation, was studied prior to the above determinations [9] and the polysaccharide derivatives actually utilised were stated to be demonstrably free from scission products of small chain-length and to have been formed to all appearance without any degradation of the original molecules. In this connexion it is to be remembered that H. Staudinger and H. Freudenberger [10] claim, on the basis of viscosity measurements, that native cellulose is more complex than the most complex of the acetates. The values are, however, put forward as the average lower limits of the size of the macromolecules, and it is not regarded as impossible that the native celluloses have molecular magnitudes of the order of the higher limit above indicated.

A method analogous to the above, employing Willstätter and Schudel's hypoiodite procedure for determining the free aldehyde groups of sugars, had previously been applied by different workers to determining the length of chain of the polysaccharides and their derivatives. This method furnished evidence that cellulose can be broken down by acetolysis to dextrins containing varying numbers of glucose units (*e.g.*, 8—13, 30—40, 20—60, etc.), but it proved to be unreliable when applied to the more complex substances, including cellulose itself.[11] H. Staudinger and H. Freudenberger place the limit of its reliability at chains of 60 glucose units,[12] but its trustworthiness up to even this degree of complexity is contested by K. Hess and his collaborators.[13] For starch a chain-length of 25—30 glucose units has been determined by its means—a value not differing greatly from the foregoing estimate; but for cellulose the corresponding value is one of only 50 units (average).[11]

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[9] For details, see the above cited papers. See also W. N. Haworth and H. R. L. Streight, *Helv. Chim. Acta*, 1932, **15**, 609; *A.*, 724; W. E. Hagenbuch, *ibid.*, p. 616; *A.*, 725.

[10] *Ber.*, 1930, **63**, [*B*], 2331; *A.*, 1930, 1416.

[11] *Ann. Reports*, 1930, **27**, 112.

Another purely chemical method which has been applied to the determination of the chain-length of celluloses from various sources relies upon the estimation of the carboxyl content of the material: [14] this is stated to be quite appreciable and to vary little with the source of the cellulose. The length of the chain is in this way assessed at 96 glucose units or a multiple thereof, whilst that of xylan, which is associated with the cellulose in wood, is similarly assessed at 16 C_5-units or a multiple thereof.

Homogeneity of Structure.—In view of the structural relationship which is held to exist between cellobiose and cellulose on the one hand and between maltose and glycogen or starch on the other, the fact that very high yields of 2 : 3 : 6-trimethyl glucose are derivable from the methylated polysaccharides would seem to preclude the possibility that polysaccharide structures are other than homogeneous chains or large rings; furthermore, the isolation of tetramethyl glucopyranose suggests very strongly that each of the structures is an *open* chain of limited length. Nevertheless there are features connected with the degradation products of the polysaccharides which are considered to throw grave doubt on the homogeneity of the molecular structures. Thus Sir J. C. Irvine maintains that when cellulose is methylated on a large scale and the product subjected to graded hydrolysis, only 2 : 3 : 6-trimethyl glucose is liberated in the first instance, the 2 : 3 : 4 : 6-tetramethyl glucose being derived from the more resistant fractions of the methylated cellulose.[15] A similar indication of non-homogeneity applies also to starch and to inulin, since it is stated in connexion with the former that one of the fractions of methylated amylose examined was convertible into a mixture of sugars which contained *as much as 23—26%* of 2 : 3 : 4 : 6-tetramethyl glucose together with 55—52% of 2 : 3 : 6-trimethyl glucose, and 21% of 2 : 3- and 2 : 6-dimethyl glucose; of the latter it is stated that a chain length of 25 or of 43 fructose units could be deduced according to whether the ω-methoxy-5-methylfurfural and trimethyl anhydrofructose produced as by-products in the hydrolysis were calculated as tetramethyl γ-fructose (total 2·7%) or not (total 1·7%).

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[12] *Ber.*, 1930, **63**, [*B*], 2331; *A.*, 1930, 1416.

[13] K. Hess, K. Dziengel, and H. Maass, *Ber.*, p. 1922; *A.*, 1930, 1416; K. Dziengel, C. Trogus, and K. Hess, *Annalen*, 1931, **491**, 52; *A.*, 1932, 47.

[14] E. Schmidt, W. Simson, and R. Schnegg, *Naturwiss.*, 1931, **19**, 1006; *A.*, 1932, 149; E. Schmidt, K. Meinel, W. Jandebeur, W. Simson, and others, *Cellulosechem.*, 1932, **13**, 129; *A.*, 934.

[15] *Nature*, 1932, **129**, 470; *Chem. and Ind.*, 1932, 263; *A.*, 502.

This question of the homogeneity of structure of wood and cotton cellulose as revealed by the composition of their hydrolysis product is considered at some length by D. J. Bell.[16] Two main considerations enter into the discussion : (1) the extent to which the hydrolytic fission of *directly* methylated celluloses differs from that of celluloses which have been acetylated as a preliminary stage in securing easy and complete methylation (the procedure employed by Haworth and Hirst and their collaborators); (2) the reason for the inertness towards hydrolytic reagents of certain resistant portions of methylated wood cellulose. Bell, like H. Staudinger and H. Freudenberger,[11] considers that acetylation treatment—especially of the kind used in the production of acetone-soluble acetates—causes extensive depolymerisation of cellulose,[17] so that the formation of an appreciable amount of tetramethyl glucose from the methylation product of the so-called "depolymerised" cellulose and none from that of so-called "intact" cellulose is accounted for; moreover, there is no necessity to assume that intact cellulose possesses an open-chain structure, since ring fission of a closed system could occur by acetolysis where acetylation is employed as a preliminary to methylation. With regard to the resistant portions of methylated wood cellulose, which are obtained both from "intact" cellulose and from cellulose which has been "depolymerised" by a preliminary acetylation process, hydrolysis is successful only after the material has been submitted to acetylation : then tri-, di-, and mono-methyl derivatives of glucose are formed and the conclusion is drawn that the inertness of the methylated material towards hydrolytic reagents is due to more fundamental reasons than degree of polymerisation, that is to say, presumably, to non-homogeneity of structure.

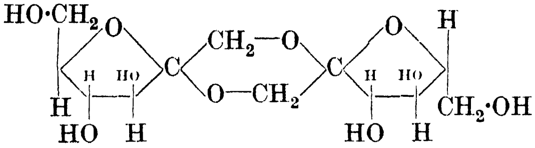
In connexion with the homogeneity of inulin it is to be noted that the very stable crystalline anhydrofructose derived by Sir J. C. Irvine and J. W. Stevenson [18] by the action of chloroformic nitric acid on

[16] *Biochem. J.*, 1932, **26**, 590, 598, 609; *A.*, 934.

[17] E. Elöd and A. Schrodt (*Z. angew. Chem.*, 1931, **44**, 933; *A.*, 1932, 48) on the contrary show by viscosity measurements that the conversion of primary cellulose acetates (insoluble in acetone) into secondary acetates (soluble in acetone) by means of acetic acid involves some deacetylation but no appreciable change in molecular aggregation.

[18] *J. Amer. Chem. Soc.*, 1929, **51**, 2197; *A.*, 1929, 1046.

inulin proves to be a difructose anhydride doubtless possessing the formula : [8, 19]



This substance, which was originally thought to represent in all probability a heterogeneous component of the inulin chain, is obtainable not only by the action of nitric acid but (in the form of its methyl derivative) by the mild hydrolysis of methylated inulin; its resistance to hydrolysis, whereby it yields fructose, is probably to be attributed to the characteristic dioxan structure of the anhydride ring. Three stereo-forms of the anhydride are theoretically capable of existence and three isomeric forms of difructose anhydride were reported last year, one of which proves to be identical with Irvine and Stevenson's compound. The formation of the anhydride appears to be brought about by rupture of the primary valencies which connect the fructose units in inulin and their reunion to form the more stable compound; at any rate there is nothing in the evidence so far adduced to show that the anhydride is pre-formed in inulin or to conflict with the view that the inulin chain is homogeneously composed of fructose units as represented in formula (XLV).

The most important evidence concerning the homogeneity or heterogeneity of structure of cellulose and starch must necessarily be derived by detailed study of degradation. Here, however, the lines of investigation are manifold, embracing the kinetics of hydrolysis, the range of possible cleavage products, and the correlation of rotational and *X*-ray data.

Degradation of Cellulose and Starch.—Degradation of cellulose or methylated cellulose to the di-, tri-, and tetra-ose stages has been definitely accomplished by acetolysis [20, 21] and hydrolysis; [22]

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[19] E. W. Bodycote, W. N. Haworth, and C. S. Woolvin, *J.*, 1932, 2389; *A.*, 1117; W. N. Haworth and H. R. L. Streight, *Helv. Chim. Acta*, 1932, **15**, 693; *A.*, 724; H. H. Schlubach and H. Elsner, *Ber.*, 1932, **65**, [*B*], 519; *A.*, 603. The last authors suggest a *mono*fructose structure.

[20] K. Freudenberg, C. C. Andersen, Y. Go, K. Friedrich, and N. W. Richtmyer, *Ber.*, 1930, **63**, [*B*], 1961; *A.*, 1930, 1412; F. Klages, *ibid.*, 1931, **64**, [*B*], 1193; *A.*, 1931, 827; W. N. Haworth, E. L. Hirst, and H. A. Thomas, *J.*, 1931, 824; *A.*, 1931, 941.

[21] K. Freudenberg, K. Friedrich, and I. Bumann, *Annalen*, 1932, **494**, 41; *A.*, 501.

[22] L. Zechmeister and G. Toth, *Ber.*, 1931, **64**, [*B*], 854; *A.*, 1931, 716.

degradation to the penta- and hexa-ose stages appears also to have been effected.[23, 21] Degradation to certain other of the simpler stages, as represented by cello*iso*biose, procellose, and the well-known " biosan " of K. Hess and H. Friese, has also been reported, but there is now little doubt that the " biosan " is a cellodextrin or mixture of cellodextrins of high molecular weight (at least 2000) and recent work shows that cello*iso*biose and procellose represent one and the same trisaccharide.[24] With regard, however, to the long series of polysaccharides which might be expected to range between hexaose and undecomposed cellulose, the most elaborate fractionations of degradation products have failed to yield pure individuals. The size of the break-down products appears to be to some extent controllable by adjusting the conditions of acetolysis, but it is remarkable that, whereas W. N. Haworth and K. Machemer,[25] like H. Staudinger,[26] K. Freudenberg,[27] K. H. Meyer and H. Mark,[28] and their respective collaborators, have found the cellodextrin acetates derived by acetolysis to be separable into groups of different average chain-length, K. Hess and his collaborators [29] have found that under comparable conditions of acetolysis the product appears to be composed of a single crystalline variety of cellulose acetate (Hess's cellulose acetate II) and one or two of the early members of the cellodextrin series.[30] The impossibility of effecting the complete separation of the few components in the latter case is attributed to the formation of additive complexes between the latter. Haworth and Machemer's results for the methylated cellodextrins, which were achieved by estimating the amount of tetramethyl methylglucoside obtainable on complete hydrolysis, differ little from those obtained directly for the cellodextrin acetates : the individual polysaccharides range in size from chains of 11 to chains of 26 glucose units.

From the acetolysis product of starch, maltotriose and maltotetraose (in addition to glucose and maltose) have been isolated in the form of their fully-methylated derivatives. In connexion with

[23] K. Hess and F. Klages, *Annalen*, 1932, **497**, 234; *A.*, 1022.

[24] W. N. Haworth, E. L. Hirst, and O. Ant-Wuorinen, *J.*, 1932, 2368; *A.*, 1116.

[25] *Ibid.*, p. 2372.

[26] *Ber.*, 1930, **63**, [*B*], 2313, 2331, 3132; *A.*, 1930, 1415, 1416; 1931, 202; *ibid.*, 1931, **64**, [*B*], 1688, 1694; *A.*, 1931, 1040.

[27] K. Freudenberg and E. Bruch, *ibid.*, 1930, **63**, [*B*], 535; *A.*, 1930, 457.

[28] K. H. Meyer and H. Mark, *ibid.*, 1928, **61**, [*B*], 2432; *A.*, 1929, 51; K. H. Meyer, H. Hopff, and H. Mark, *ibid.*, 1930, **63**, [*B*], 1531; *A.*, 1930, 1025.

[29] K. Dziengel, C. Trogus, and K. Hess, *Annalen*, 1931, **491**, 52; *A.*, **1932**, 47.

[30] These lower polysaccharides, including the bioses, trioses, tetraoses, etc., derived from cellulose and starch, have been conveniently termed by K. Freudenberg, " oligosaccharides."

these substances and the corresponding oligosaccharides from cellulose, K. Freudenberg and his collaborators [21] point out that if the molecular rotation, $[M]_n$, of a polysaccharide of n units be represented as the sum of the rotations due to the two (aldehydic and non-aldehydic) end units, $[M]_a$ and $[M]_e$, respectively and to $n—2$ intermediate units each furnishing a rotation-contribution of $[M]_\infty/\infty$ (this differing little from that due to the middle unit of a pentasaccharide), there is justification for writing the resulting expression, $[M]_n = [M]_a + (n - 2)[M]_\infty/\infty + [M]_e$, in the form $[M]_n = [M]_2 + (n - 2)[M]_\infty/\infty$, or, to show the average contribution of one unit of the chain, in the form

$$\frac{[M]_n}{n} = [M]_2 - \frac{[M]_\infty}{\infty} + \frac{2(n-1)}{n}\left(\frac{[M]_\infty}{\infty} - \frac{[M]_2}{2}\right).$$

The difficulty which attends the application of the expression to the calculation of the rotation of the higher polysaccharides, owing to complication arising from the existence of α- and β-forms, is fully recognised ; the values calculated for the trioses and tetraoses by employing the observed values for the relevant bioses and hexaoses are in good agreement with the experimental values obtained under equilibrium conditions in various solvents ; moreover, the value of 0—3° calculated for cellulose in water is a credible one.

The progress of the hydrolysis of cellulose with 50% sulphuric acid has been measured by titration with iodine, and from the results values for K_1 and K_2, the hydrolysis constants concerned respectively in the initial rupture of the intact chain and in the final stage of hydrolysis (cellobiose to glucose), have been calculated.[31] Now, of all the possible assumptions that might be made in terms of these constants as to the course of hydrolysis of the cellulose molecule (*e.g.*, that K_1 is the hydrolysis constant applicable to the fission of all glucosidic linkages present in the molecule of triose, tetraose and so on up to cellulose, and K_2 is the hydrolysis constant of cellobiose), it is shown, on the basis of certain calculations of W. Kuhn [32] as to the form of various alternative hydrolysis curves, that only two are reconcilable with the observed changes in the value of the velocity constant as hydrolysis proceeds : of these two, only one is definitely supported by independent values for the velocity constant obtained by following the course of reaction polarimetrically. This assumption is that K_1 represents the hydrolysis constant of the tetraose and all higher fragments up to cellulose, and K_2 the constant of cellobiose and cellotriose. Obviously this represents only an approximation to the truth, since if cellulose be conceived as a long chain molecule a number of transition values must actually lie between the hydrolysis constant applicable to degradation of the long fragments (K_1) and that concerned in the last step (K_2). (Thus, although K_2 is attributed to both the biose and the triose, the triose will possess a lower mean constant than K_2, and the tetraose and pentaose a higher constant than K_1.) Nevertheless, provided Kuhn's fundamental expressions are accepted,[33] the experimental results afford striking evidence as to the uniformity of the linkages throughout the cellulose chain.

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[31] K. Freudenberg, W. Kuhn, W. Dürr, F. Bolz, and G. Steinbrunn, *Ber.*, 1930, **63**, [*B*], 1510; *A.*, 1930, 1025; compare K. H. Meyer, H. Hopff, and H. Mark, *ibid.*, 1929, **62**, [*B*], 1103; 1930, **63**, [*B*], 1531; *A.*, 1929, 799; 1930, 1025.

[32] *Ibid.*, p. 1503; *A.*, 1930, 1025.

Starch behaves in the same manner as cellulose, but its constants are higher and the difference between K_1 and K_2 is smaller than in the case of cellulose.[31] Owing to the latter fact distinction between the long-chain formula and a biose anhydride formula for starch would have been impossible without other evidence. In this connexion the fact that starch yields nearly 100% of maltose during diastatic hydrolysis appears at first sight to be in opposition to the conception of the former as a chain of 1 : 4-linked α-glucose units; but this observation probably only means that the enzyme attacks one end of the chain in much the same way that the oxidation of cellulose chains is held to occur.[34]

Some interest attaches to the group of simple polysaccharide anhydrides derived from starch by the action of F. Schardinger's bacillus,[35] although the formation of these has no clear bearing on the constitution of starch. Two of the anhydrides originally recognised by H. Pringsheim [36] in Schardinger's α-dextrin now appear to be identical (the supposed diamylose is the same as the tetra-amylose);[37] but more interesting is the fact that *X*-ray examination of α-amylose (amylopectin) is stated to show the existence of six distinct modifications which differ in *X*-ray pattern and are capable of interconversion either in solution or during the transformation of solvent-containing forms into solvent-free ones.[38] The nature of the molecular changes in starch and cellulose and their derivatives which are responsible for these modifications of the *X*-ray diagrams are at present obscure. The water-soluble oligosaccharides (tetraose, pentaose, and hexaose) derived by acetolysis of cellulose are stated to give the same interferences as hydrocellulose,[39] whilst the native and mercerised forms of cellulose as well as a number of modifications of starch are all reported to show quite distinctive *X*-ray diagrams.[40] It is suggested, indeed, that three or four truly isomeric forms of cellulose and four or five such forms of starch exist, the isomerism being of a steric nature, due to the pliation of the pyranose rings.

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[33] See the contention of F. Klages, *Ber.*, 1932, **65**, [*B*], 302; *A.*, 370; see also the reply of K. Freudenberg and W. Kuhn, *ibid.*, p. 484; *A.*, 501.

[34] T. Nakashima, *J. Soc. Chem. Ind. Japan*, 1931, **34**, 414; *A.*, 1932, 149.

[35] *Centr. Bakt. Par.*, 1911, ii, **29**, 188; *A.*, 1911, i, 181.

[36] *Ber.*, 1912, **45**, 2533 and subsequent papers; *A.*, 1912, i, 832; see also H. Pringsheim, A. Weidinger, and P. Ohlmeyer, *ibid.*, 1931, **64**, [*B*], 2125; *A.*, 1931, 1277.

[37] A. Miekeley, *ibid.*, 1930, **64**, [*B*], 1957; 1932, **65**, [*B*], 69; *A.*, 1930, 1414; 1932, 255; M. Ulmann, *Biochem. Z.*, 1932, **251**, 458; *A.*, 1021; K. Hess and M. Ulmann, *Naturwiss.*, 1932, **20**, 296; *A.*, 724. See, however, H. Pringsheim, A. Weidinger, and H. Sallentien, *Ber.*, 1931, **64**, [*B*], 2117; *A.*, 1931, 1276.

[38] M. Ulmann, C. Trogus, and K. Hess, *ibid.*, 1932, **65**, [*B*], 682; *A.*, 604.

Cellulose, starch, inulin, mannan, xylan, silk fibroin, wool, horn, etc., are all reported to be broken down to mixtures of low-molecular anhydrides by the action of dry hydrogen chloride.[41] It is suggested that addition compounds with the reagent are first formed, and these, being more susceptible of degradation than the original compounds, yield small molecules (possibly unimolecular) which subsequently revert to a more or less highly polymerised condition. Degradation of cellulose acetate to the condition of a water-soluble carbohydrate has been effected by benzenesulphonic acid,[42] and that of starch to gentiobiose by heating with dilute hydrochloric acid under pressure.[43] In the latter case the disaccharide would appear to be a reversion product of glucose, but its formation by direct scission of a polysaccharide in the α-amylose portion of the starch is the view recorded.

With respect to the amylose and amylopectin portions of starch, although the former is generally regarded as constituting the major portion of the starch grain, it is now stated that the yields of amylopectin derived by the action of dilute methyl-alcoholic hydrogen chloride on different starches range from 63 to 83%. The amylopectin thus obtained, while probably not identical with the natural sheath substance of the grains, is claimed to be (unlike former preparations) free from amylose.[44]

Synthesis of Cellulose.—The action of bacteria in building up substances of polysaccharide character from sugar-containing materials has long been observed. Now, however, it is shown that the membranous material produced by the action of *Acetobacter xylinum* on glucose behaves in all its observed physical and chemical properties (including rotation, X-ray structure, acetylation, methylation, and hydrolysis) as a true cellulose.[45]

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[39] K. Hess and F. Klages, *Annalen*, 1932, **497**, 234; *A.*, 1022.

[40] J. R. Katz and A. Weidinger, *Rec. trav. chim.*, 1932, **51**, 842; *A.*, 934.

[41] H. H. Schlubach, H. Elsner, and V. Prochovnick, *Angew. Chem.*, 1932, **45**, 245; *A.*, 502.

[42] H. Pringsheim and K. Ward, jun., *Cellulosechem.*, 1932, **13**, 65; *A.*, 502.

[43] T. C. Taylor and D. Lifschitz, *J. Amer. Chem. Soc.*, 1932, **54**, 1054; *A.*, 500.

[44] A. Eckert and A. Marzin, *J. pr. Chem.*, 1932, [ii], **133**, 110; *A.*, 370.

E. H. Farmer.

Part II.—Homocyclic Division.

Tautomerism.

(Continued from *Ann. Reports*, 1931, **28**, 105.)

Three-carbon Systems.—The work on the influence of structure on tautomerism in three-carbon systems terminated by one activating group, of the general type

$$(\text{I.})\quad >\!\text{CH}\cdot\overset{|}{\text{C}}\text{:CRX} \qquad\qquad >\!\text{C:}\overset{|}{\text{C}}\cdot\text{CHRX}\quad(\text{II.})$$

$$\alpha\beta\text{-form} \qquad\qquad\qquad \beta\gamma\text{-form}$$

$$(\text{X} = \text{CO}_2\text{H, CO}_2\text{Et, CN, or COMe})$$

is now reaching finality inasmuch as all the more accessible systems have been examined, and it is of interest to review the results in the light of the theoretical considerations advanced to explain them.

The application of the electronic theory to this problem, originally proposed by Ingold, Shoppee, and Thorpe [1] and used in these Reports, was extended by R. P. Linstead,[2] who pointed out that the influence of steric factors and the effect of conjugation (Lapworth and Manske's " Thiele factor ") [3] must be taken into account in addition to the polar factor. The theory in that form gives a satisfactory explanation of the interconversion of unsaturated acids (I and II ; $X = CO_2H$) or, more strictly, their anions in alkali.*

Thus, the introduction of an alkyl group in the α-position retards tautomeric change and causes a shift of the equilibrium towards the αβ-form ; an alkyl group introduced into the γ-position causes a marked shift in the opposite direction without affecting the mobility, that is, the rate at which equilibrium is established ; and an alkyl group in the β-position also favours the βγ-form. The

[45] H. Hibbert and J. Barsha, *J. Amer. Chem. Soc.*, 1931, **53**, 3907 ; *A.*, 1931, 1401 ; *Canadian J. Res.*, 1931, **5**, 580 ; *A.*, 1932, 256 ; E. Schmidt, M. Atterer, and H. Schnegg, *Cellulosechem.*, 1931, **12**, 235 ; *A.*, 1931, 1038.

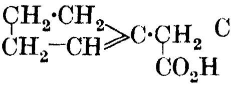
[1] *J.*, 1926, 1477 ; *A.*, 1926, 939.

[2] *J.*, 1929, 2498 ; *A.*, 1930, 64 ; compare *Ann. Reports*, 1931, *loc. cit.*

[3] *J.*, 1928, 2535 ; *A.*, 1928, 1245.

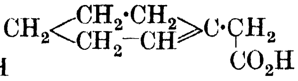
* The statement that the interconversion of acids is studied "in sodium ethoxide at 25° " (*Ann. Reports*, 1931, **28**, 108) should read " with 10 equivalents of 25% potassium hydroxide solution at 100°." The footnote on the same page refers to the equilibration of the ester, not the acid.—G. A. R. Kon.

principal discrepancy is the position of equilibrium in the cyclic acids, in which the βγ-form is favoured in every case :



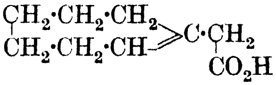
$\begin{matrix}CH_2\cdot CH_2\\ CH_2-CH\end{matrix}\!>\!C\cdot CH_2\cdot CO_2H$

85% βγ at equil.
(III.)



$CH_2\!<\!\begin{matrix}CH_2\cdot CH_2\\ CH_2-CH\end{matrix}\!>\!C\cdot CH_2\cdot CO_2H$

88% βγ
(IV.)



$\begin{matrix}CH_2\cdot CH_2\cdot CH_2\\ CH_2\cdot CH_2\cdot CH\end{matrix}\!>\!C\cdot CH_2\cdot CO_2H$

67% βγ
(V.)

this will be discussed below.

In nitriles (I and II; X = CN) the equilibrium is largely influenced by the great tendency of the cyano-group to become part of a conjugated system : this was again observed in a recent investigation.[4] This conjugative effect accounts for the fact that, of all the unsaturated nitriles examined, only two are preferentially stable in the βγ-form. These are *iso*hexenonitrile (VI)[4] and phenylcrotononitrile (VII)[5] : the former owes its stability to the

(VI.) $CMe_2{:}CH\cdot CH_2\cdot CN$ $\qquad$ $CHPh{:}CH\cdot CH_2\cdot CN$ (VII.)

polar effect of the γ-alkyl group, and in the latter the phenyl group exercises a strong conjugative influence opposed to that of the nitrile group.

In nitriles, therefore, the effect of a β-alkyl group is negligible; but a γ-group produces its normal effect, doubtless because it acts *directly* on one of the carbon atoms concerned in tautomerism.

Unsaturated nitriles have also been the subject of repeated study by Bruylants and his school,[6] but mainly from the stereochemical point of view. In his latest paper[7] Bruylants criticises some of Letch and Linstead's conclusions, more especially as regards the purity of the nitriles prepared by different processes and the value of the analytical methods employed by the two schools; these differences in no way affect the main conclusions discussed above.*

In unsaturated ketones (I and II; X = COMe), although the effect of β- and γ-substituents on tautomerism accords well with theory, that of an α-alkyl group, founded on numerous observations,[8] causes not only a great diminution of mobility but also a pronounced shift in equilibrium towards the βγ-form, that is, in the opposite sense to that predicted by theory. Moreover, remarkable differences, not predictable from considerations of polarity, are observed between the different cyclic derivatives : [9]

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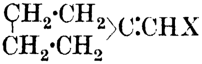
[4] R. A. Letch and R. P. Linstead, *J.*, 1932, 443; *A.*, 371.

[5] A. Kandiah and R. P. Linstead, *J.*, 1929, 2139; *A.*, 1929, 1294.

[6] P. Bruylants, *Bull. Soc. chim. Belg.*, 1930, **39**, 572; R. Breckpot, *ibid.*, p. 462; P. Colmant, *ibid.*, p. 568; G. Heim, *ibid.*, p. 458; *A.*, 1931, 472, 194, 472, 205; P. Bruylants and H. Minetti, *Bull. Acad. roy. Belg.*, 1930, **16**, 1116; P. Bruylants, *ibid.*, 1931, **17**, 1008; P. Bruylants and L. Ernould, *ibid.*, p. 1027; *A.*, 1931, 205, 1403; A. Dewael, *Bull. Soc. chim. Belg.*, 1932, **41**, 318, 324; J. Baerts, *ibid.*, p. 314; G. Festraete, *ibid.*, p. 327; P. Bruylants, *ibid.*, p. 333; *A.*, 1119.

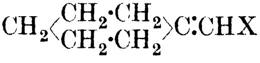
[7] P. Bruylants, *ibid.*, p. 309; *A.*, 1119.

* Dr. Linstead informs the Reporter that a re-examination of the nitriles used in Letch and Linstead's work leaves no doubt as to their purity; Bruylants's criticism on this point appears to be based on a misunderstanding.



$\begin{array}{l}CH_2{\cdot}CH_2\\ CH_2{\cdot}CH_2\end{array}\!>C{:}CHX$

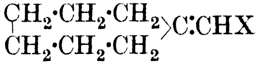
77% αβ at equil.



$CH_2\!<\!\begin{array}{l}CH_2{\cdot}CH_2\\ CH_2{\cdot}CH_2\end{array}\!>C{:}CHX$

23% αβ

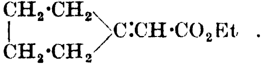
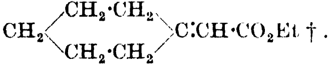
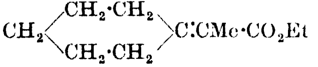
(X = COMe)



$\begin{array}{l}CH_2{\cdot}CH_2{\cdot}CH_2\\ CH_2{\cdot}CH_2{\cdot}CH_2\end{array}\!>C{:}CHX$

40% αβ

Finally, the equilibria in a representative series of unsaturated esters have been examined ; [10] these follow in the main the rules laid down for acids, but ethyl *cyclo*pentylideneacetate constitutes an exception to this, the equilibrium favouring the αβ-compound as in the corresponding ketone ; the compound is also exceptionally mobile, apparently a characteristic of all *cyclo*pentane derivatives. The effect of the α-alkyl group is irregular, for it favours the βγ-form in the *cyclo*hexane derivative but in no other case.

Ester (αβ-form).	Equilibrium (% αβ).	Mobility.
$CHMe_2{\cdot}CH{:}CH{\cdot}CO_2Et$ *	10 (?)	High
$CH_2Et{\cdot}CH{:}CH{\cdot}CO_2Et$	92 (?)	153
$CH_2Et{\cdot}CH{:}CMe{\cdot}CO_2Et$	95	151
$CMeEt{:}CH{\cdot}CO_2Et$	75	26
$CMeEt{:}CMe{\cdot}CO_2Et$	95	2
 $\begin{array}{l}CH_2{\cdot}CH_2\\ CH_2{\cdot}CH_2\end{array}\!>C{:}CH{\cdot}CO_2Et$	60	835
 $CH_2\!<\!\begin{array}{l}CH_2{\cdot}CH_2\\ CH_2{\cdot}CH_2\end{array}\!>C{:}CH{\cdot}CO_2Et$ †	38	8·1
$\begin{array}{l}CH_2{\cdot}CH_2\\ CH_2{\cdot}CH_2\end{array}\!>C{:}CMe{\cdot}CO_2Et$	88	84
 $CH_2\!<\!\begin{array}{l}CH_2{\cdot}CH_2\\ CH_2{\cdot}CH_2\end{array}\!>C{:}CMe{\cdot}CO_2Et$	5	0·15

* Linstead, *J.*, 1929, 2498. † Kon and Linstead, *J.*, 1929, 1269.

It is difficult to account satisfactorily for these anomalies.

An attempt was made to explain [11] the preferential existence of *cyclo*hexane derivatives in the βγ-form by assuming that the wandering of the double bond into the ring relieves the strain in the six-membered ring which is postulated by Baeyer's strain theory. Conversely, it has been suggested by Bennett (*Ann. Reports*, 1929, **26**, 118) that the greater stability of the αβ-form in *cyclo*pentane derivatives is due to the fact that the migration of the double bond into the five-membered ring introduces a strain: a particularly good example of this difference is afforded by the substituted malonic acids (VIII) and (IX); the former exists exclusively in the αβ- and the latter in the βγ-form and their respective isomerides do not appear to be capable of isolation.[12] *

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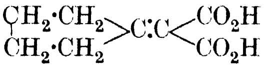
[8] G. A. R. Kon and E. Leton, *J.*, 1931, 2496; *A.*, 1931, 1274; compare *Ann. Reports*, 1931, **28**, 109.

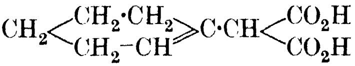
[9] *Ann. Reports*, 1929, **26**, 117. The figures given above are the latest available; Kon, *J.*, 1930, 1616; *A.*, 1930, 1184.

[10] G. A. R. Kon, R. P. Linstead, and G. W. G. Maclennan, *J.*, 1932, 2454; *A.*, 1111.

[11] S. F. Birch, G. A. R. Kon, and W. S. G. P. Norris, *J.*, 1923, **123**, 1361; G. A. R. Kon and E. A. Speight, *J.*, 1926, 2727; *A.*, 1926, 1246.

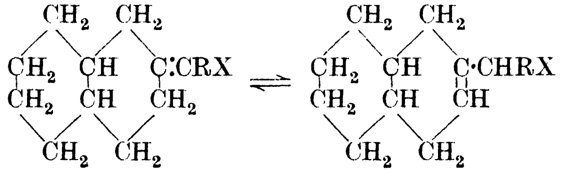
(VIII.) 

$$\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}\!>C{:}C<\begin{matrix}CO_2H\\ CO_2H\end{matrix}$$

 (IX.)

$$CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2-CH\end{matrix}\!\geqslant C\cdot CH<\begin{matrix}CO_2H\\ CO_2H\end{matrix}$$

The equilibria in the monocarboxylic acids (III), (IV), and (V), however, cannot be reconciled with these views. In addition, the foundation for them has been considerably weakened by the observations of R. S. Thakur [13] on a number of dicyclic acids, ketones, and esters of the type (X) and (XI). He finds that

(X.)  (XI.)

β-decalin derivatives behave in all respects like the corresponding *cyclo*hexane compounds, the figures in the two series agreeing within a few units %:

X = CO_2H: R = H, 88% βγ at equil.; R = Me, —% βγ at equil.
X = COMe: R = H, 63% βγ at equil.; R = Me, 100% βγ at equil.
X = CO_2Et: R = H, 60% βγ at equil.; R = Me, 90% βγ at equil.

The anomalous effect of the α-alkyl group is again observed.

In the corresponding *trans*-hexahydrohydrindene derivatives of the general type (XII) and (XIII), Thakur [14] finds that the equilibrium is in every case, including the monocarboxylic acids, on the side of the αβ-form; the compounds display even greater mobility than *cyclo*pentane derivatives.

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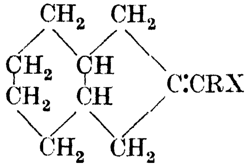
[12] W. E. Hugh and G. A. R. Kon, *J.*, 1930, 775; *A.*, 1930, 1162.

[13] *J.*, 1932, 2129, 2139; *A.*, 1032.

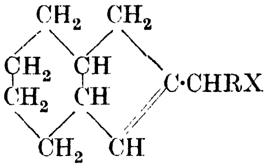
[14] *Ibid.*, pp. 2147, 2157; *A.*, 1032.

* The statement (*Ann. Reports*, 1931, **28**, 110) that the ester of the acid (VIII), when regenerated from its sodio-derivative, contains 30—50% of the βγ-isomeride is erroneous. The original authors did not give an estimate of its βγ-content, but the ester appeared from its physical properties to be practically pure ethyl *cyclo*pentenylmalonate; this view is confirmed by unpublished experiments.

(XII.)



(XIII.)



With regard to the decalin derivatives, the results may be summed up by saying that the effect of the *cyclo*hexane ring remains the same even when the ring becomes part of the dicyclic system.

The strainless nature of the decalin system is now generally accepted, although there is not the same measure of agreement regarding the simple *cyclo*hexane ring. If the latter is strainless, no difficulty arises in the interpretation of the striking similarity between *cyclo*hexane and decalin derivatives, but this means that the " strain factor " originally postulated has no existence. If, on the other hand, the single ring is regarded as strained, it must be inferred that this strain has no influence on tautomerism, unless it be assumed that the decalin system is strained to the same extent. It appears preferable, therefore, to abandon for the present all attempts to correlate ring strain with tautomerism.

A similar argument applies to the *cyclo*pentane and hexahydrohydrindene compounds. The ring system of the former is strainless and should not, therefore, differ in a radical manner in its influence on tautomerism from the decalin system. The resemblance between *cyclo*pentane and hexahydrohydrindene compounds is not unexpected; the ring system of the latter appears from models to be slightly strained (in the *trans*-form), but this strain is in the opposite sense to that in the planar six-membered ring. The great tendency of these compounds to exist in the αβ-form might therefore be held to support Bennett's view (see above), since the entrance of the double bond into the ring would tend to produce an even more strained condition than that present in *cyclo*pentenyl derivatives, just as the facts require.

The Glutaconic Acids.—Some progress has been made in the investigation of three-carbon systems terminated by activating groups at both ends of the general type

$$X{\cdot}CHR{\cdot}CR'{:}CR''X \quad \text{and} \quad X{\cdot}CR{:}CR'{\cdot}CHR''X$$

(X may be CO_2H, CO_2Et, or CN; R, R' and R'' may be alkyl or aryl groups, CO_2H, or CO_2Et)

A brief reference to the subject has already been made in the *Report* for 1931, p. 111; further investigations published in the course of the year serve to establish several generalisations regarding the simpler glutaconic acids.[15–20] An unsymmetrically substituted glutaconic acid, such as α-benzylglutaconic acid, can theoretically exist in two isomeric forms (I) and (II), each of which can give rise to two stereoisomerides :

$CO_2H\cdot C(CH_2Ph){:}CH\cdot CH_2\cdot CO_2H$ (I.) *aβ*-Acid (*cis* and *trans*)

$CO_2H\cdot CH(CH_2Ph)\cdot CH{:}CH\cdot CO_2H$ (II.) *βγ*-Acid (*cis* and *trans*)

In practice two forms are usually encountered, namely, the *cis*-form of the αβ-acid and the *trans*-form of the βγ-acid, the remaining two isomerides being comparatively unstable; Kon and Watson[18] have, however, converted the *cis*-αβ-form of α-benzyl-β-methylglutaconic acid into its *trans*-stereoisomeride by ultraviolet irradiation.

The relative stabilities of the two more stable modifications vary widely according to the nature of the substituents present; *e.g.*, α-benzylglutaconic acid is stable in its *trans*-βγ-form, and the *cis*-αβ-form is converted into this even on treatment with warm water and therefore represents a true " labile " modification.[18] The same is probably true of other simple α-substituted acids; the *cis*-form of glutaconic acid itself has only lately been obtained[21] and is also extremely unstable. The α-benzyl-β-methyl acids (III) and (IV) are both stable, but the *cis*-acid passes integrally into its isomeride on treatment with alkali, and the reverse change is brought about by acids; we therefore have one alkali-stable and one acid-stable form :[1, 4]

$$CO_2H\cdot C(CH_2Ph){:}CMe\cdot CH_2\cdot CO_2H \underset{\text{acid}}{\overset{\text{alkali}}{\rightleftharpoons}} CO_2H\cdot CH(CH_2Ph)\cdot CMe{:}CH\cdot CO_2H$$

(III.) *cis* (*αβ*)

(IV.) *trans* (*βγ*)

These acids thus differ from the majority of tautomeric compounds in which the equilibrium is independent of the reagent employed and incidentally provide an interesting example of the conversion of a *trans*- into a *cis*-acid by the agency of hydrochloric acid, a reagent commonly used to bring about the reverse change.

Similar relationships obtain in the β-phenyl-α-methylglutaconic acids;[19] the presence of a phenyl group exercises the expected

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[15] G. A. R. Kon and E. M. Watson, *J.*, 1932, 1; *A.*, 252.

[16] B. S. Gidvani, G. A. R. Kon, and C. R. Wright, *ibid.*, p. 1027; *A.*, 601.

[17] G. A. R. Kon and H. R. Nanji, *ibid.*, p. 2426; *A.*, 1127.

[18] G. A. R. Kon and E. M. Watson, *ibid.*, p. 2434; *A.*, 1127.

[19] B. S. Gidvani and G. A. R. Kon, *ibid.*, p. 2443; *A.*, 1127.

[20] G. A. R. Kon and H. R. Nanji, *ibid.*, p. 2557; *A.*, 1247.

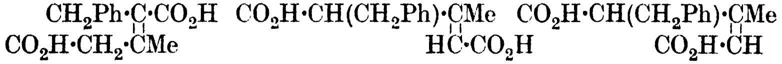
[21] I. R. Malachowski, *Ber.*, 1929, **62**, [*B*], 1323; *A.*, 1929, 794.

stabilising influence (owing to its ± T effect) on *both* possible forms (V) and (VI): this is exemplified by the isolation, though in small

$$CO_2H{\cdot}CMe{:}CPh{\cdot}CH_2{\cdot}CO_2H \quad \text{(V.)} \qquad CO_2H{\cdot}CHMe{\cdot}CPh{:}CH{\cdot}CO_2H \quad \text{(VI.)}$$

amount, of a third acid which appears to be the *cis*-modification of (VI).

The stability of the different forms of unsymmetrically substituted acids appears to depend largely on steric factors in addition to the expected polar effects and it has been suggested [18] that the symmetrical distribution of groups about the doubly-bound carbon atoms is the principal one, thus:

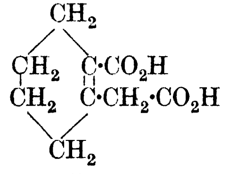


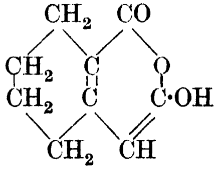
$$\begin{array}{c} CH_2Ph{\cdot}C{\cdot}CO_2H \\ \| \\ CO_2H{\cdot}CH_2{\cdot}CMe \end{array} \qquad \begin{array}{r} CO_2H{\cdot}CH(CH_2Ph){\cdot}CMe \\ \| \\ HC{\cdot}CO_2H \end{array} \qquad \begin{array}{r} CO_2H{\cdot}CH(CH_2Ph){\cdot}CMe \\ \| \\ CO_2H{\cdot}CH \end{array}$$

Stable Stable Unstable

An investigation of some cyclic glutaconic derivatives [3] shows that ability to exist in stereoisomeric forms is not essential to "glutaconic character." The acid (VII) is just like an ordinary disubstituted glutaconic acid; it forms an enolic anhydride (VIII), its ester yields a stable potassio-derivative, and the latter can be converted into the α-methyl ester (IX). These properties are therefore solely connected with the existence of a mobile hydrogen atom. The acid (VII) and its ester and also the analogous *cyclo*pentane derivatives only exist in one form, no sign of the expected isomerides with the double bond outside the ring, such as (X), having been encountered.

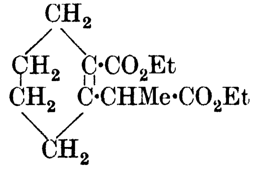
(VII.)

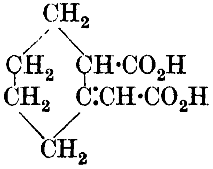




(VIII.)

(IX.)

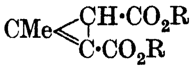




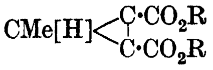
(X

A similar behaviour might have been anticipated in the acid (XI) and its ester, in which all three carbon atoms of the three-carbon chain are included in the ring:

(XI.)



$$CMe\!<\!\begin{array}{l} CH{\cdot}CO_2R \\ | \\ C{\cdot}CO_2R \end{array}$$

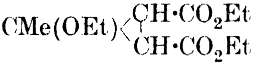


$$CMe[H]\!<\!\begin{array}{l} C{\cdot}CO_2R \\ | \\ C{\cdot}CO_2R \end{array}$$

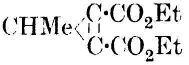
(XII.)

Some of the reactions of these substances were indeed originally held to support such a view, although the " normal " formulation (XII) was adopted for the acid and its solid ester.[22]

A reinvestigation of the whole subject has led to some unexpected conclusions.[23] The ester, which is correctly represented by (XI), does not possess a mobile hydrogen atom in the ordinary sense and the supposed formation of a sodio-derivative cannot be substantiated. The action of sodium ethoxide on this ester causes the rapid addition of ethyl alcohol to the double bond to give the ethoxy-ester (XIII) and no evidence has been obtained of the existence of the Δ^1-isomeride (XIV) of the ester (XI). The most remarkable fact ascertained relates to the action of heat on the ester (XI), which was stated to give rise to the " labile " modification, formulated as (XI) by the earlier workers. This has now been shown to consist of the straight-chain acetylenic ester (XV), the change involving not only the opening of the *cyclo*propane ring but the absorption of the methyl group into the chain.


$\mathrm{CMe(OEt)}<\begin{matrix}\mathrm{CH\cdot CO_2Et}\\ |\\ \mathrm{CH\cdot CO_2Et}\end{matrix}$

(XIII.)

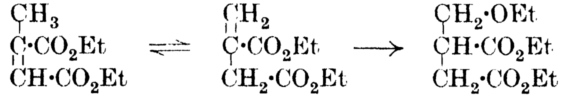

$\mathrm{CHMe}<\begin{matrix}\mathrm{C\cdot CO_2Et}\\ \|\\ \mathrm{C\cdot CO_2Et}\end{matrix}$

(XIV.)

$\mathrm{CO_2Et\cdot C{:}C\cdot CH_2\cdot CH_2\cdot CO_2Et}$

(XV.)

The behaviour of the ester (XI) with sodium ethoxide recalls the reaction of the esters of itaconic, citraconic, and mesaconic acids, which all undergo conversion into the same ethoxy-ester, directly derived from itaconic ester : [24]


$$\begin{matrix}\mathrm{CH_3}\\ |\\ \mathrm{C\cdot CO_2Et}\\ \|\\ \mathrm{CH\cdot CO_2Et}\end{matrix}\;\rightleftharpoons\;\begin{matrix}\mathrm{CH_2}\\ \|\\ \mathrm{C\cdot CO_2Et}\\ |\\ \mathrm{CH_2\cdot CO_2Et}\end{matrix}\;\longrightarrow\;\begin{matrix}\mathrm{CH_2\cdot OEt}\\ |\\ \mathrm{CH\cdot CO_2Et}\\ |\\ \mathrm{CH_2\cdot CO_2Et}\end{matrix}$$

(*cis* and *trans*) Itaconic ester ω-Ethoxymethylsuccinic ester

It has, however, been shown that an equilibrium mixture of all three unsaturated esters is produced and that the two stereoisomeric $\alpha\beta$-esters (citraconic and mesaconic) predominate in this; it is clearly unsafe to conclude that the equilibrium in this case favours the $\beta\gamma$-form (ethyl itaconate) because derivatives of the latter, such as the ethoxy-ester and the addition product with ethyl sodiomalonate, are preferentially produced,[25] for additions are known to be influenced by such factors as the solubility of the sodio-derivatives formed.

The carbethoxyglutaconic esters [16] are generally similar to the corresponding cyanoglutaconic esters [26] in occurring as mixtures of αβ- and βγ-isomerides,

---

[22] F. R. Goss, C. K. Ingold, and J. F. Thorpe, *J.*, 1923, **123**, 327, 3342; 1924, **125**, 1927; 1925, **127**, 460.

[23] G. A. R. Kon and H. R. Nanji, *J.*, 1932, 2557; *A.*, 1247.

[24] E. H. Coulson and G. A. R. Kon, *J.*, 1932, 2568; *A.*, 1234.

[25] C. W. Shoppee, *J.*, 1930, 968; *A.*, 1930, 912.

$$\underset{(\alpha\beta)}{(CO_2Et)_2C{:}CR{\cdot}CHR'{\cdot}CO_2Et} \qquad \underset{(\beta\gamma)}{(CO_2Et)_2CH{\cdot}CR{:}CR'{\cdot}CO_2Et}$$

from which the βγ-forms can usually be obtained in the pure state by conversion into the potassium derivatives (which always have the βγ-structure; no abnormal cases have been encountered) and acidification with a weak acid in the absence of water.* Ethyl α-carbethoxy-β-phenylglutaconate gives rise to two different metallic derivatives: [16, 19] the yellow, sparingly soluble sodio-derivative obtained in the condensation of ethyl sodiomalonate with ethyl phenylpropiolate appears to have the structure (XVI), whereas that formed from the ester itself on treatment with sodium ethoxide has the sodium attached to the other end of the chain (XVII). A compound similar to (XVI) is also formed from ethyl

$$\underset{(XVI.)}{(CO_2Et)_2C{\cdot}CPh{\cdot}CH{\cdot}CO_2Et\}Na} \qquad \underset{(XVII.)}{Na\{(CO_2Et)_2C{\cdot}CPh{\cdot}CH{\cdot}CO_2Et}$$

sodiomethylmalonate and ethyl phenylpropiolate, a fact which should have a considerable bearing on the mechanism of the Michael reaction, since it can be proved that in this case it is the sodium and not the methyl group of the addendum which separates and becomes attached to the negatively polarised end of the unsaturated molecule.

The cyanoaconitic esters[26a] are difficult to purify and do not lend themselves to detailed study; in general, however, they behave like the cyanoglutaconic esters, particularly in forming abnormal γ-alkyl derivatives: [26]

$$\begin{array}{ll} (XVIII.) & CO_2Et{\cdot}CH(CN){\cdot}C(CO_2Et){:}CH{\cdot}CO_2Et \longrightarrow \\ (XIX.) & CO_2Et{\cdot}C(CN){:}C(CO_2Et){\cdot}CHR{\cdot}CO_2Et \end{array}$$

The sodio-derivative of the ester (XVIII) must also be derived from the isomeric αβ-ester, and a product consisting mainly of the latter is obtained on acidification.

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[26] G. A. R. Kon and H. R. Nanji, *J.*, 1931, 560; *A.*, 1931, 608; compare *Ann. Reports*, 1931, **28**, 111.

[26a] R. D. Desai, *J.*, 1932, 1088; *A.*, 602.

* The repeated observation of such "false equilibria" lends strong support to the view that the anionic charge originally localised on one or other end of the three-carbon system (in the sodio-derivative) need not *necessarily* be redistributed and therefore lead to an equilibrium mixture when the mobile hydrogen atom is reintroduced by acidification. This redistribution appears to take place under the influence of the acid (or water) and is analogous to the phenomenon discussed on p. 146, namely, the selective reaction of benzylmagnesium chloride to give α- or γ-reaction products according to the reactant employed.

Methyleneazomethine Systems.—The effect of different meta-substituents on the mobility [27] in the system

$$\mathrm{R\cdot C_6H_4\cdot CH{:}N\cdot CH_2Ph} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{R\cdot C_6H_4\cdot CH_2\cdot N{:}CHPh}$$

follows the order of the dipole moment of the compound R·Ph more closely than was the case with the corresponding para-compounds,[28] in agreement with theoretical considerations. Similarly, the agreement between the effect on mobility and side-chain reactivity is closer in the meta- than in the para-series. The effect of different groups on equilibrium should follow their effect in facilitating meta-substitution, but as all the groups employed (except NO_2) are *op*-directing, a comparison is impossible and their effect on side-chain reactivity is therefore employed.

Anionotropy.—Comparatively little work has been carried out on this subject. A. Kirrmann and R. Rambaud [29] have found that acetylation of the ester (I) with acetic anhydride leads to the corresponding acetate (II), but if the hydroxy-compound is treated with phosphorus tribromide, the bromine enters the γ-, not the α-position; the bromide (III) on treatment with sodium acetate gives an acetate (IV), isomeric with (II).

(I.) $\mathrm{CH_2{:}CH\cdot CH(OH)\cdot CO_2Et}$ $\mathrm{CH_2{:}CH\cdot CH(OAc)\cdot CO_2Et}$ (II.)
(III.) $\mathrm{CH_2Br\cdot CH{:}CH\cdot CO_2Et}$ $\mathrm{CH_2(OAc)\cdot CH{:}CH\cdot CO_2Et}$ (IV.)

R. Rambaud [30] subsequently found that the α-bromide isomeric with (III) was also produced but passed into (III) on distillation. The corresponding methyl ester undergoes the change even more readily, but the α-chloro-ester can be prepared in the pure state and is stable; on treatment with calcium bromide, however, the γ-bromide alone is produced.

Some abnormal cases of the Grignard reaction have been interpreted on the assumption of an anionotropic mechanism. Cinnamyl chloride (V) gives a magnesium derivative which is converted by carbon dioxide into the acid (VI),[31] and this is explained by the migration of the MgCl residue from the γ- to the α-carbon atom:

$$\text{(V.)}\ \mathrm{CHPh{:}CH\cdot CH_2Cl} \longrightarrow [\mathrm{CHPh{:}CH\cdot CH_2^-} \rightleftharpoons \mathrm{{}^-CHPh\cdot CH{:}CH_2}] + \mathrm{MgCl^-}$$

$$\text{(VI.)}\ \mathrm{CHPh(CO_2H)\cdot CH{:}CH_2} \longrightarrow \mathrm{CPh(CO_2H){:}CHMe}\ \text{(VII.)}$$

---

[27] C. W. Shoppee, *J.*, 1932, 696; *A.*, 384.

[28] *Idem, J.*, 1930, 968; 1931, 1225; *A.*, 1930, 912; 1931, 834; *Ann. Reports*, 1931, **28**, 106.

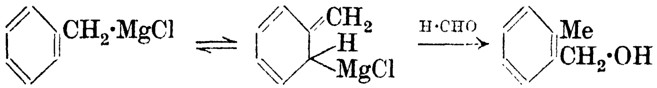
[29] *Compt. rend.*, 1932, **194**, 1168; *A.*, 600.

[30] *Ibid.*, **195**, 389; *A.*, 930.

[31] H. Gilman and S, A. Harris, *J. Amer. Chem. Soc.*, 1931, **53**, 3541; *A.*, 1931, 1290.

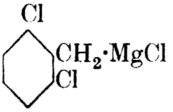
The acid (VI) readily undergoes further change with acids or alkalis, or merely on heating, into methylatropic acid (VII), this time by a prototropic mechanism. The formation of the intermediate ions or free radicals accords well with the isolation of αδ-diphenyl-$\Delta^{\alpha\epsilon}$-hexadiene[32] as a by-product in the above reaction, since this can result from the union of the two different radicals.

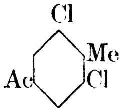
The reaction of benzylmagnesium chloride with formaldehyde, giving *o*-tolylcarbinol, is interpreted on similar lines,[33] the three-carbon system here involving the phenyl group :



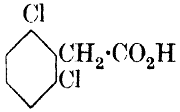
The two forms are probably in equilibrium, because the action of carbon dioxide on the Grignard reagent gives the normal product, phenylacetic acid.

A somewhat similar explanation is advanced by P. R. Austin and J. R. Johnson,[34] who find that the course of the reaction is dependent on the nature of the compound reacting with the Grignard reagent; for instance, *o*-tolyl derivatives tend to be produced from acid chlorides, anhydrides, formaldehyde, and its derivatives: it is suggested that these influence the production of one or other electromeric form of the benzyl radical, which then reacts. The tautomeric change can involve the *p*-position of the benzyl group if both *o*-positions are substituted, leading to αε-migration of the MgCl group; thus the Grignard reagent from 2 : 6-dichlorobenzyl chloride gives with acetyl chloride 3 : 5-dichloro-4-methylacetophenone (VIII), although with carbon dioxide the normal product, 2 : 6-dichlorophenylacetic acid (IX), is obtained :





(VIII.)



(IX.)

The migration of a $PhSO_2$ ion is held by D. T. Gibson[35] to explain the production of the compound (XI) from benzenesulphonylacetone (X) and methyl *p*-toluenethiolsulphonate :[36]

$$\text{(X.)}\quad Ph{\cdot}SO_2{\cdot}CH_2{\cdot}COMe + C_6H_4Me{\cdot}SO_2{\cdot}SMe \longrightarrow$$
$$C_6H_4Me{\cdot}SO_2{\cdot}CH(SMe){\cdot}COMe \quad \text{(XI.)}$$

and the compound (XI) can be converted into the corresponding benzenesulphonyl derivative by means of methyl benzenethiolsulphonate in excess; the excess of $PhSO_2$ or $C_6H_4Me{\cdot}SO_2$ ions determines the course of the reaction, but the presence of the SMe group is shown to be essential for the exchange to occur. The thiol groups are also readily exchanged, such as SMe for SEt, in compounds of the type (XI). The exchange of groups here is essentially intermolecular and differs in this respect from the majority of tautomeric changes in which the separation of the mobile group is generally inferred rather than proved.

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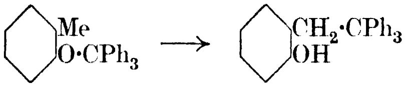
[32] H. Gilman and S. A. Harris, *J. Amer. Chem. Soc.*, 1932, **54**, 2072; *A.*, 730.
[33] H. Gilman and J. E. Kirby, *ibid.*, p. 348; *A.*, 410.
[34] *Ibid.*, p. 647; *A.*, 385.
[35] *J.*, 1932, 1819; *A.*, 837.
[36] *Idem, J.*, 1931, 2641; *A.*, 1931, 1394.

Further cases of tautomerism are discussed on pp. 173, 174.

Other Rearrangements.—Owing to limitation of space the discussion is deferred of a number of interesting papers on the pinacol–pinacolin change,[37] on pinacolinic deamination,[38] and on the rearrangement of quaternary ammonium salts[39] and of *o*-hydroxy- and *o*-amino-arylsulphones.[40]

A remarkable example of group migration is provided by triphenylmethyl *o*-tolyl ether,[41] the displaced group entering the side chain :



The constitution of the product has been confirmed by G. S. Parsons and C. W. Porter.[42]

Terpenes.

Progress in this group of natural products continues, especially in the elucidation of the structure of the more complex compounds of the sesqui- and di-terpene group; the new investigations bear remarkable testimony to the usefulness of the so-called "isoprene hypothesis," which has frequently led to the prediction of the correct structure when the experimental evidence was indecisive.

In the monoterpene group few major problems remain to be solved, and of these the ever-green question of camphene has lately undergone some notable developments.

S. Nametkin and L. Brüssoff[43] have found that α-methylcamphene (II), obtained by the dehydration of *tert.*-methylfenchyl alcohol (I) or of *tert.*-methylborneol,[44] is hydrated to a methyl*iso*borneol which is not the 6-methyl compound (III) that should be formed by the usual Wagner mechanism, but the isomeric 4-methyl compound (IV); it gives on dehydration, in addition to α-methylcamphene, the isomeric β-methylcamphene (V), and this is readily reconverted into 4-methyl*iso*borneol:

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[37] M. Tiffeneau, J. Lévy, and collaborators, *Bull. Soc. chim.*, 1931, [iv], **49**, 1595 *et seq.*; W. E. Bachmann and F. H. Moser, *J. Amer. Chem. Soc.*, 1932, **54**, 1124; *A.*, 515; W. E. Bachmann, *ibid.*, pp. 1969, 2112; *A.*, 745, 737; C. H. Beale and H. H. Hatt, *ibid.*, p. 2405; *A.*, 854.

[38] A. McKenzie and J. R. Myles, *Ber.*, 1932, **65**, [*B*], 209; *A.*, 382; A. McKenzie and (Miss) E. M. Luis, *ibid.*, p. 794; *A.*, 746.

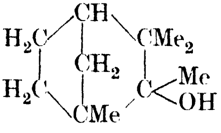
[39] T. Thomson and T. S. Stevens, *J.*, 1932, 55; *A.*, 262; J. L. Dunn and T. S. Stevens, *ibid.*, p. 1926; *A.*, 816.

[40] L. A. Warren and S. Smiles, *ibid.*, pp. 1040, 2774; *A.*, 735; A. A. Levi and S. Smiles, *ibid.*, p. 1488; *A.*, 735.

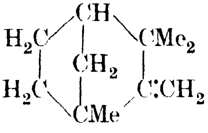
[41] P. Schorigin, *Ber.*, 1926, **59**, [*B*], 2506; *A.*, 1927, 54.

[42] *J. Amer. Chem. Soc.*, 1932, **54**, 363; *A.*, 267.

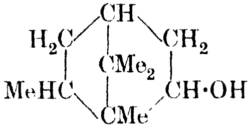
[43] *Annalen*, 1927, **459**, 144; *A.*, 1928, 182.



(I.)

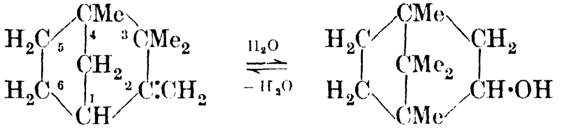


(II.)



(III.)

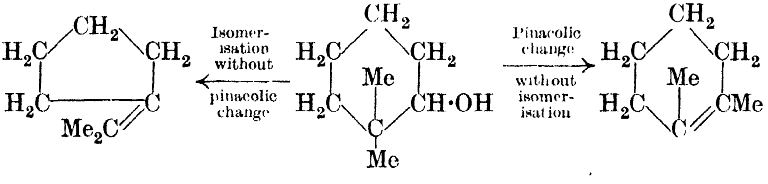
(V.)



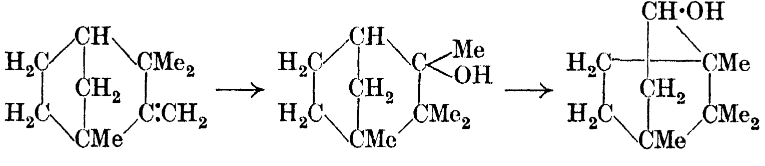
(IV.)

The structure of the new products is definitely established and has been independently confirmed by later work;[45] and a similar series of reactions has also been carried out starting with *tert.*-phenylbornyl alcohol.[46]

These facts cannot be explained by the usual (Wagner) mechanism of the camphene change and the explanation advanced is that, just as dehydration of 2 : 2-dimethyl*cyclo*hexanol can take place *without* change of ring structure but is then accompanied by the wandering of a methyl group (Meerwein),



so the reverse process also can take place; in this way α-methylcamphene is hydrated as follows,



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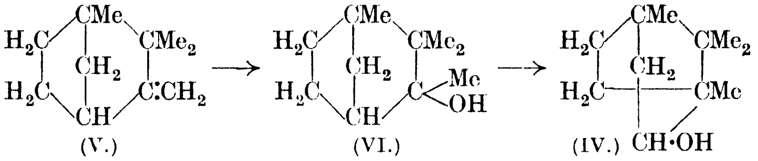
[44] L. Ruzicka, *Helv. Chim. Acta*, 1918, **1**, 110; *A.*, 1918, i, 398; S. Nametkin and M. Schlesinger, *J. Russ. Phys. Chem. Soc.*, 1919, **51**, 144.

[45] M. Bredt-Savelsberg and J. Buchkremer, *Ber.*, 1931, **64**, 600; *A.*, 1931, 625; S. Nametkin and L. Brüssoff, *J. pr. Chem.*, 1932, **135**, 155.

[46] S. Nametkin, A. Kitschkin, and D. Kurssanoff, *J. pr. Chem.*, 1930, **124**, 144; *A.*, 1930, 216.

the camphene hydrate then passing into the more stable methyl*iso*borneol.

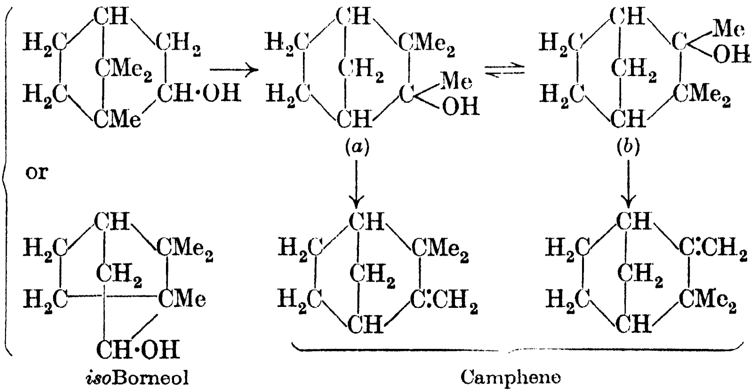
Now in the hydration of β-methylcamphene this pinacolic change does not take place; owing to the fact that in this compound a CH group is present next to the $C{:}CH_2$ group, the intermediate camphene hydrate (VI) can be formed by the simple addition of water to the double bond:


(V.) (VI.) (IV.)

This simplified mechanism cannot apply to α-methylcamphene, because it would lead to an unstable tertiary alcohol; the primary addition product first undergoes a pinacolic change *without* isomerisation of the ring, followed by the conversion of the β-methylcamphene hydrate into 4-methyl*iso*borneol.

The dehydration of the latter yields, as already stated, mainly β-methylcamphene formed by the simplified process; some α-methylcamphene is, however, produced at the same time, evidently by a reversal of the sequence of changes just described, thus confirming the reality of *both* reaction mechanisms.

When these considerations are applied to camphene itself, it is clear that both processes must lead to the same final product; thus, the dehydration of *iso*borneol must give rise to camphene:


*iso*Borneol Camphene

There are, however, implications in these changes which appear to have escaped the original authors, and these have since been pointed out.[47] For instance, the two formulæ of camphene given above are not identical but represent mirror images (owing to the two rings not being in the same plane). Moreover, different products will be formed according as the methyl and the hydroxyl group which are interchanged are *cis* or *trans* to one another. In the former case there will be a reversal of the sign of rotation; in the latter, the *trans*-isomeride will be formed, having the same sign of rotation as the initial material:

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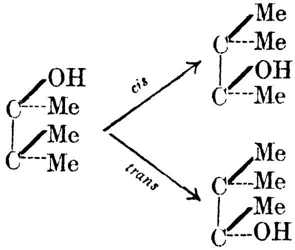
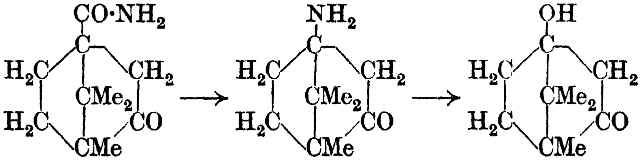
[47] J. Houben and E. Pfankuch, *Annalen*, 1931, **489**, 193; *A.*, 1931, 1300.



both the products belong to the opposite optical system from that of the initial material. Owing to the symmetrical nature of the bridge heads in camphene these changes involve a change not of structure but merely of optical properties; thus, in the reversible conversion of camphene through the hydrochloride into *iso*bornyl chloride, the two forms corresponding to (*a*) and (*b*) would be in equilibrium and equal quantities of *d*- and *l*-product should be formed, leading to complete racemisation, which is actually observed. The same process accounts for the racemisation of *iso*bornyl chloride in boiling cresol. A similar mechanism explains the production[48] of active camphene from bornyl chloride and aniline under mild conditions, whereas the inactive hydrocarbon is formed under more drastic conditions.

When one of the bridge heads in camphene or its derivatives carries a substituent, the Nametkin change leads to isomerisation as in the case of methylcamphene, as well as to optical inversion: this has been well illustrated by Houben and Pfankuch[47] by a number of examples. For instance, *l*-camphorcarboxylic acid was prepared from *d*-camphor, its amide (VII) converted into the amine, and the latter into 4-hydroxycamphor (VIII):



(VII.) (VIII.)

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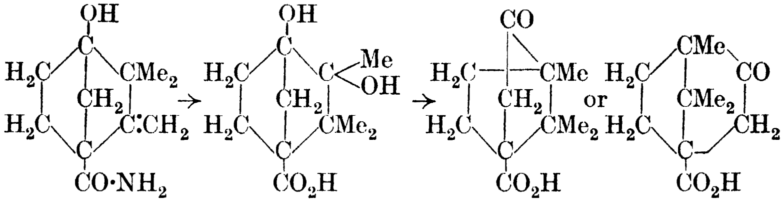
[48] P. Lipp and G. Stutzinger, *Ber.*, 1932, **65**, [*B*], 241; *A.*, 398.

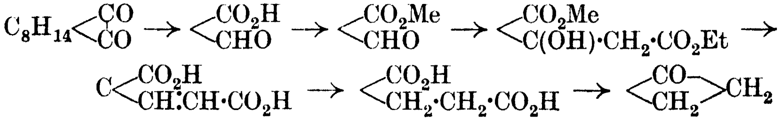
From the latter the amide of 4-hydroxycamphenecarboxylic acid (IX) was obtained, which on hydrolysis with hydrochloric acid underwent addition of water, the product suffering the Nametkin change at the same time, and finally forming camphorcarboxylic acid (XI) itself. The complete cycle thus involves the conversion of the *l*- into the *d*-acid :



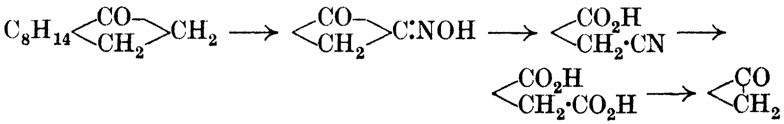
(IX.) (X.) (XI.)

In a later paper[49] the conversion of *d*-camphor into its antipode is described (*via* camphor dichloride, 4-chloro*iso*borneol, 4-chlorocamphor, and the reduction of the semicarbazone of the latter) : this supplies a proof of the reaction mechanism proposed by Nametkin, not depending on racemisation phenomena.

In connexion with camphor chemistry, the preparation of *d*-β-homocamphor by the following series of reactions should be noted :[50]


$$C_8H_{14}{<}\begin{matrix}CO\\CO\end{matrix} \rightarrow {<}\begin{matrix}CO_2H\\CHO\end{matrix} \rightarrow {<}\begin{matrix}CO_2Me\\CHO\end{matrix} \rightarrow {<}\begin{matrix}CO_2Me\\C(OH){\cdot}CH_2{\cdot}CO_2Et\end{matrix} \rightarrow$$
$$C{<}\begin{matrix}CO_2H\\CH{:}CH{\cdot}CO_2H\end{matrix} \rightarrow {<}\begin{matrix}CO_2H\\CH_2{\cdot}CH_2{\cdot}CO_2H\end{matrix} \rightarrow {<}\begin{matrix}CO-\\CH_2\end{matrix}{>}CH_2$$

The strongly dextrorotatory β-homocamphor was then converted into β-camphor[51] (epicamphor), which was lævorotatory :


$$C_8H_{14}{<}\begin{matrix}CO-\\CH_2\end{matrix}{>}CH_2 \longrightarrow {<}\begin{matrix}CO-\\CH_2\end{matrix}{>}C{:}NOH \longrightarrow {<}\begin{matrix}CO_2H\\CH_2{\cdot}CN\end{matrix} \longrightarrow$$
$${<}\begin{matrix}CO_2H\\CH_2{\cdot}CO_2H\end{matrix} \longrightarrow {<}\begin{matrix}CO\\CH_2\end{matrix}$$

An interesting experiment from the point of view of the " isoprene hypothesis " is that of T. Wagner-Jauregg,[52] who treated isoprene with acetic acid containing a little sulphuric acid. Amongst the condensation products were geraniol, *cyclo*geraniol, linalool and α-terpineol, 1 : 4- and 1 : 8-cineole, and a monocyclic sesquiterpene hydrocarbon with three double bonds, convertible by formic acid into a dicyclic one of the caryophyllene group.

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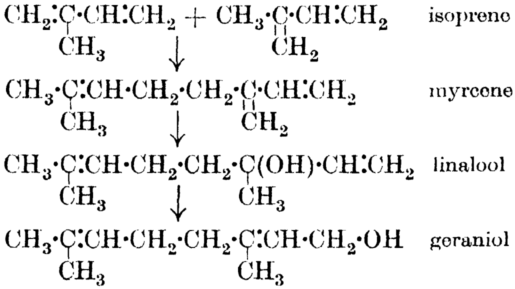
[49] J. Houben and E. Pfankuch, *Ber.*, 1931, **64**, [*B*], 2719; *A.*, 1932, 62.
[50] F. Salmon-Legagneur, *Compt. rend.*, 1931, **192**, 748; *A.*, 1931, 626.
[51] *Idem*, *ibid.*, 1932, **194**, 467; *A.*, 399.
[52] *Annalen*, 1932, **496**, 52; *A.*, 856.

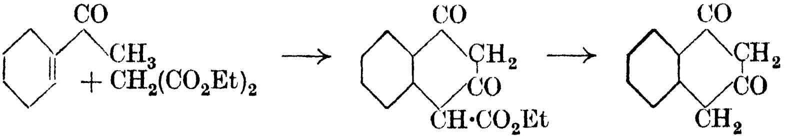
The original hypothesis was that 1 : 4-dimerisation of isoprene residues would take place, followed by hydration, and the formation of geraniol seems to support such a view. In acid solution, however, linalool is known to give geraniol, and this process may account for its formation thus :



$$\begin{array}{ll}
CH_2{:}\underset{CH_3}{C}\cdot CH{:}CH_2 + CH_3\cdot\underset{CH_2}{\overset{}{C}}\cdot CH{:}CH_2 & \text{isoprene}\\
\downarrow & \\
CH_3\cdot\underset{CH_3}{C}{:}CH\cdot CH_2\cdot CH_2\cdot\underset{CH_2}{C}\cdot CH{:}CH_2 & \text{myrcene}\\
\downarrow & \\
CH_3\cdot\underset{CH_3}{C}{:}CH\cdot CH_2\cdot CH_2\cdot\underset{CH_3}{C}(OH)\cdot CH{:}CH_2 & \text{linalool}\\
\downarrow & \\
CH_3\cdot\underset{CH_3}{C}{:}CH\cdot CH_2\cdot CH_2\cdot\underset{CH_3}{C}{:}CH\cdot CH_2\cdot OH & \text{geraniol}
\end{array}$$

Sesquiterpenes.—The notable progress in this group is principally due to the researches of L. Ruzicka, who has attacked the problem in a broad and fundamental manner. In order to place beyond doubt the identity of some of the naphthalene derivatives obtained by the dehydrogenation of polyterpenes, he has synthesised all the possible trimethylnaphthalenes ;[53] the synthesis of some important phenanthrene derivatives, including pimanthrene and retene, was, however, carried out by R. D. Haworth, B. M. Letsky, and C. R. Mavin,[54] and L. Ruzicka and H. Waldmann[55] have independently synthesised pimanthrenequinone. An interesting synthesis of phenanthrenes is also due to J. C. Bardhan and S. C. Sengupta,[56] who have obtained pimanthrene, retene, and 1 : 4-dimethylphenanthrene.

For comparison with naturally occurring hydronaphthalene derivatives, decalin and all the possible methyldecalins have been prepared[57] by a method which is an extension of that originally used[58] for the preparation of decalin-1 : 3-dione :



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[53] L. Ruzicka and H. Ehmann, *Helv. Chim. Acta*, 1932, **15**, 140; *A.*, 277.

[54] *J.*, 1932, 1784, 2720; R. D. Haworth, *ibid.*, p. 1125; R. D. Haworth and F. M. Bolam, *ibid.*, p. 2248; *A.*, 839, 608, 1024.

[55] *Helv. Chim. Acta*, 1932, **15**, 907; *A.*, 948.

[56] *J.*, 1932, 2520, 2798; *A.*, 1241.

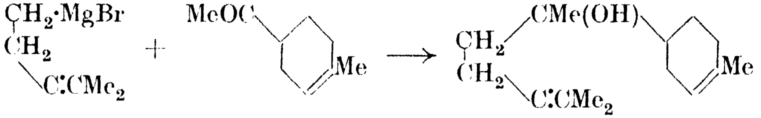
[57] L. Ruzicka, D. R. Koolhaas, and A. H. Wind, *Helv. Chim. Acta*, 1931, **14**, 1151, 1171; *A.*, 1931, 1302.

[58] G. A. R. Kon and M. Qudrat-i-Khuda, *J.*, 1926, 3071; *A.*, 1927, 150.

The diketone undergoes reduction by Clemmensen's method to the saturated hydrocarbon, which is found to belong to the *trans*-series—another illustration of the remarkable ease with which the *trans*-locking of the second ring occurs.

A comparison of the physical properties of the dicyclic sesquiterpenes and their fully saturated reduction products with the synthetic decalins shows that the former all belong to the *cis*-series.

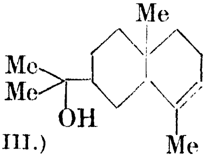
Bisabolol and bisabolene trihydrochloride have been synthesised as follows : [59] β-terpineol was ozonised, giving the ketone (I), which was condensed with the Grignard reagent from ε-bromo-β-methyl-Δ^{β}-pentene, giving bisabolol (II), converted into a trihydrochloride identical with that prepared from nerolidol :



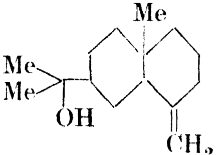
(I.) (II.)

This synthesis removes all doubt as to the position of the double bonds, which formerly rested on analogy.

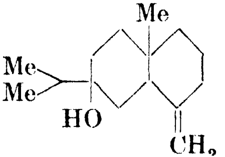
The structure of eudesmol may now be considered as settled.[60] The formula (III) was regarded as probable,[61] although the alternative (IV) had not been finally disposed of :



(III.)
α-form



β-form



(IV.)

A hydroxyl group attached to a side chain is much more readily benzoylated than one directly connected to the ring; [62] it is now found that eudesmol readily gives a benzoyl derivative. If eudesmol is correctly represented by formula (III), the dihydrochlorides of eudesmene and of selinene should be identical or, at most, stereoisomeric, and this has now been confirmed; the dihydrochloride of selinene exists in two stereoisomeric forms, m. p. 52° and 74°, respectively. The final proof of the position of the hydroxyl in eudesmol was obtained by dehydrating dihydroeudesmol under very mild conditions; the hydrocarbon (V) was then almost exclusively produced, and gave acetyldimethyldecalin (VI) on ozonisation :

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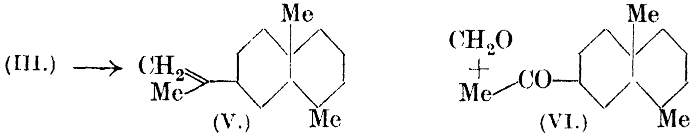
[59] L. Ruzicka and M. Liguori, *Helv. Chim. Acta*, 1932, **15**, 3; *A.*, 277.

[60] L. Ruzicka, A. H. Wind, and D. R. Koolhaas, *ibid.*, 1931, **14**, 1132; *A.*, 1931, 1302.

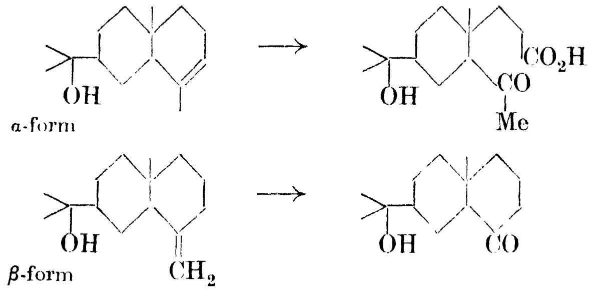
[61] L. Ruzicka and E. Capato, *Annalen*, 1927, **453**, 62; *A.*, 1927, 570.

[62] L. Ruzicka and A. G. van Veen, *ibid.*, 1929, **476**, 109; *A.*, 1929, 1305.



The formation of the *iso*propylidene analogue of (V), previously observed,[61] was inconclusive, since this could have been formed from an eudesmol of the structure (III) or (IV).

Eudesmol, however, is a mixture of α- and β-forms, for oxidation products of both have been obtained from it :



The α-form, which gives rise to acidic products on ozonisation, is principally found in eudesmol prepared from selinene dihydrochloride (Semmler and Risse's selinenol),[63] since elimination of hydrogen chloride usually tends to produce the form with the double bond in the ring; the β-form predominates in the natural product (from the oil of *Eucalyptus Macarthuri*). The melting point and rotation of eudesmol do not appear to be notably affected by its composition.

Several alcohols of the sesquiterpene series, such as machilol,[64] cryptomeradol,[65] and the alcohol from the bark of *Magnolia Ovata*,[66] are identical with eudesmol.[67]

Of more than passing interest is the discovery of three crystalline ketones closely related to eudesmol, which have been isolated from the wood oil of *Eremophila Mitchelli*, since they are amongst the first cyclic ketones of the sesquiterpene series so far discovered; moreover, their structure has been completely elucidated.[68] They are eremophilone (VII), 2-hydroxyeremophilone (VIII), and 2-hydroxy-1:2-dihydroeremophilone (IX):

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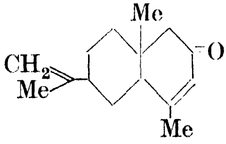
[63] *Ber.*, 1912, **45**, 3305; *A.*, 1913, i, 66.

[64] S. Takagi, *J. Pharm. Soc. Japan*, 1921, **41**, 473; *A.*, 1921, i, 721.

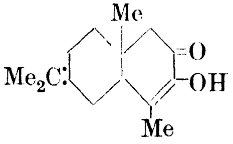
[65] H. Wienhaus and H. Scholtz, *Ber. Schimmel and Co.*, 1929, 267; *A.*, 1929, 1308.

[66] Y. Sugii and H. Shindo, *J. Pharm. Soc. Japan*, 1930, **50**, 103; *A.*, 1931, 267.

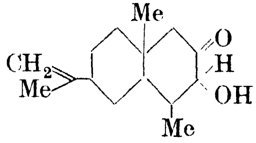
[67] L. Ruzicka, D. R. Koolhaas, and A. H. Wind, *Helv. Chim. Acta*, 1931, **14**, 1151; *A.*, 1931, 1302.



(VII.)

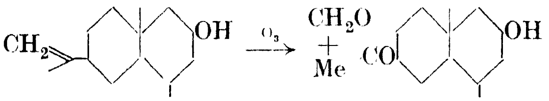


(VIII.)

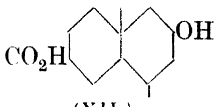


(IX.)

Eremophilone is dehydrogenated by selenium to eudalene and contains two double bonds, one of which is αβ- to the keto-group, since it forms an unstable addition product with hydrogen sulphide and an oxide with hydrogen peroxide; the formation of a hydroxymethylene compound shows that there is a CH_2 group next to the keto-group, *i.e.*, the system $\vdots CH{\cdot}CO{\cdot}CH_2-$. In accordance with this, reduction with sodium and alcohol leads to dihydroeremophilol (X), which on ozonisation yields formaldehyde and a hydroxyketone, $C_{14}H_{24}O_2$ (XI), further oxidised by hypobromite to an acid, $C_{13}H_{22}O_3$ (XII):



(X.) (XI.)



(XII.)

The double bond which escapes reduction and is here shown to be in the side chain, must be independent of the conjugated system $\vdots CH{\cdot}CO{\cdot}CH_2{\cdot}$ and the latter must therefore be situated in the ring *not* carrying the *iso*propenyl group. Only two such positions are available and a decision between that adopted and the alternative with the keto-group in position 2 can readily be made. Thus, the oxide of eremophilone on treatment with acetic acid and sodium acetate passes into 2-hydroxyeremophilone, identical with the natural product (VIII). The benzoate of the latter gives acetone and only a trace of formaldehyde on ozonisation and must therefore consist largely of the *iso*propylidene compound; in eremophilone and its derivatives we are clearly dealing with another case of isomerism such as that of eudesmol discussed above. Apart from acetone, the principal oxidation product is a mixed anhydride (XIII), formed by cyclisation of the original oxidation product with loss of water :

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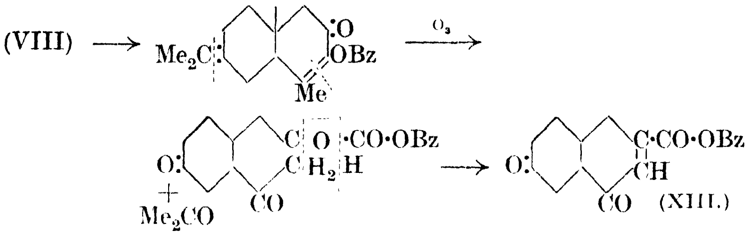
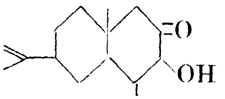
[68] A. E. Bradfield, A. R. Penfold, and J. L. Simonsen, *J.*, 1932, 2744. A. Pfau (*Helv. Chim. Acta*, 1932, **15**, 1481) claims to have isolated two isomeric ketones, $C_{15}H_{20}O$, from oil of cedar and another closely related compound from oil of turmeric, but no experimental details are available.

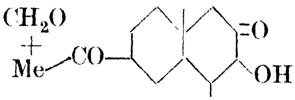


The formation of this neutral compound finally establishes the position of the ketonic group in these compounds. The compound (VIII) is evidently analogous to diosphenol in the monoterpene series.

2-Hydroxy-1 : 2-dihydroeremophilone is oxidised by ozone to formaldehyde, a ketone (XIV), and only a trace of acetone; this compound, like the parent ketone, consists mainly of the *iso*propenyl form :



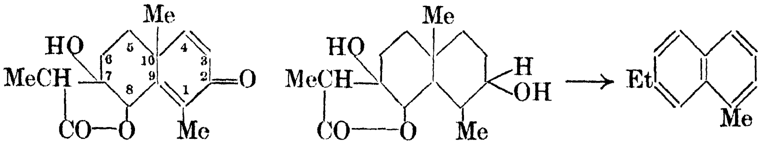
(IX.)



(XIV.)

The position of the keto-group must be the same as in the parent compound, because 2-hydroxytetrahydroeremophilone, which is obtained from (IX) on catalytic reduction, can be further reduced with sodium amalgam to tetrahydroeremophilone, in the same way that hydroxycamphor is reduced to camphor;[69] and the tetrahydro-compound is oxidised by hydrogen peroxide to a dibasic acid $C_{15}H_{24}O_4$, showing that the hydroxyl group is next to the carbonyl.

Artemisin.—Artemisin, which accompanies santonin in *Artemisia Marina*, has been proved to be 7-hydroxysantonin (I).[70] Energetic reduction in the presence of platinum oxide gives hexahydroartemisin (II), which is dehydrogenated to 1-methyl-7-ethylnaphthalene :



(I.) (II.)

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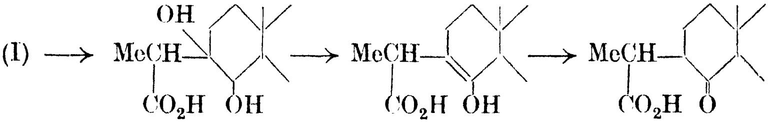
[69] J. Bredt and M. Bredt-Savelsberg, *Ber.*, 1929, **62**, [*B*], 2214; *A.*, 1929, 1308.

[70] K. Tettweiler, O. Engel, and E. Wedekind, *Annalen*, 1932, **492**, 105; *A.*, 271.

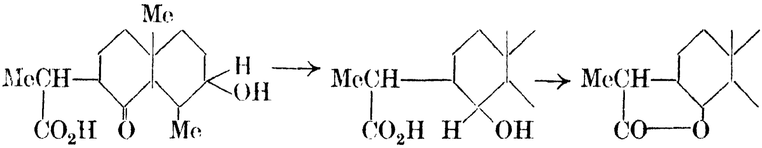
The formation of desmotropoartemisin, which is a true phenol,[71] shows that both the double bonds must be in the same ring; and they must occupy the positions shown, because artemisin does not react with Caro's acid and therefore has no CH_2 group next to the carbonyl.

The hydroxyl group in artemisin is tertiary and its position is shown by hydrolysis with alkali, artemionic acid (III) being formed:



(III.)

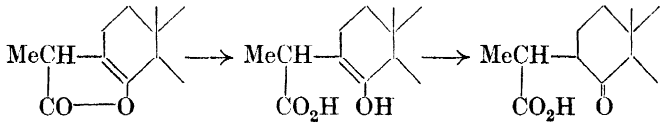
This acid can be hydrogenated to a tetrahydro-compound, which can also be obtained by alkaline hydrolysis of α-tetrahydroartemisin (there are four of these, as required by theory), and is further reduced by sodium amalgam to hexahydrosantonin (IV):



(IV.)

The hydroxyl group of artemisin can be eliminated by heating with formic acid, artemisene (V) being formed; and this on opening the lactone ring passes into artemionic acid (VI), thus confirming the mode of reaction given above:

(V.)



(VI.)

Helenin.—Helenin, the bitter principle of elecampane root, is related to santonin and contains a mixture of lactones, in which alantolactone and *iso*alantolactone were identified many years ago;[72] K. W. F. Hansen,[73] and L. Ruzicka and P. Pieth [74] have in addition isolated dihydro*iso*alantolactone, identical with the product obtained by reduction by Sprinz.[75] The lactones are accompanied in the original oil by sesquiterpenes which belong to the eudesmol group, being dehydrogenated to eudalene by heating with selenium.[76]

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[71] P. Bertolo, *Gazzetta*, 1923, **53**, 867; *A.*, 1924, i, 304.

[72] J. Kallen, *Ber.*, 1876, **9**, 154; *A.*, 1876, i, 917.

[73] *Ber.*, 1931, **64**, [*B*], 67, 943; *A.*, 1931, 360, 734.

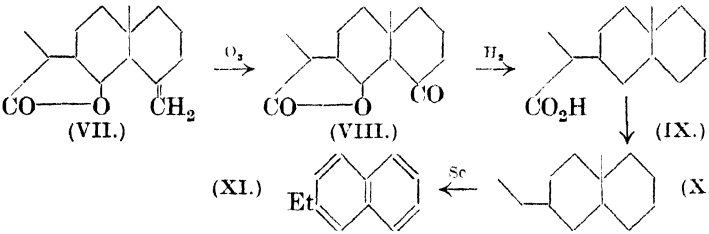
[74] *Helv. Chim. Acta*, 1931, **14**, 1090; *A.*, 1931, 1301.

[75] *Ber.*, 1901, **34**, 775; *A.*, 1901, i, 325.

[76] L. Ruzicka and J. A. van Melsen, *Helv. Chim. Acta*, 1931, **14**, 397; *A.*, 1931, 734.

The lactones are dehydrogenated to 1-methyl-7-ethylnaphthalene and evidently differ only in the position of the double bonds, because they are reduced to the same tetrahydro-derivative, very similar to, but not identical with, deoxytetrahydrosantonin, with which it is probably stereoisomeric.[77]

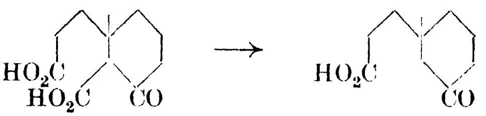
The naturally occurring dihydro-lactone gives on ozonisation a keto-lactone, also obtained by K. W. F. Hansen,[77] which on reduction by Clemmensen's method gives an acid, $C_{14}H_{24}O_2$, and a hydrocarbon : the latter, also obtained by decarboxylation of the acid, is 9-methyl-3-ethyl-*cis*-decalin [78] and yields β-ethylnaphthalene when heated with selenium. These changes are formulated as follows :



(VII.) (VIII.) (IX.) (X.) (XI.)

β-Ethylnaphthalene has also been obtained from the dihydrolactone by Hansen, but by a more direct and therefore less instructive route. These reactions establish the carbon skeleton present in the two lactones.

The position of the carboxyl and carbinol groups can be inferred from the fact that ozonisation, followed by mild oxidation with permanganate, of a mixture of alantolactone and *iso*alantolactone gives the acid (XII).[76]

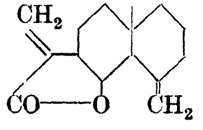


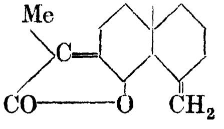
(XII.)

Unstable intermediate compound.

Both lactones are readily reduced to dihydro-derivatives, which suggests that one of the double bonds is in the αβ-position to the carbonyl group. This would give rise to formulæ (XIII) and (XIV) for the *iso*-lactone :

(XIII.)





(XIV.)

As the dihydro-derivatives and dihydrochlorides of the two lactones are different, the double bond not adjacent to the carbonyl group must also be differently situated in the two isomerides. Ozonisation of dihydroalantolactone gives a ketonic acid (XV), showing that the double bond in question is situated in the ring. The addition of hydrogen chloride to this double bond must inevitably produce an arrangement identical with that resulting from the semicyclic *iso*-lactone; and as the two dihydrochlorides are different, they must be represented by the formulæ (XVI) and (XVII). The two lactones therefore most probably have the structures (XIII) and (XVIII):

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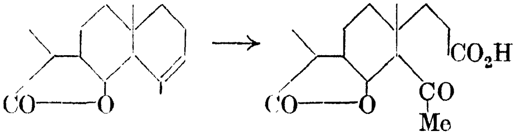
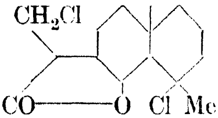
[77] *Ber.*, 1931, **64**, [*B*], 1904; *A.*, 1065.

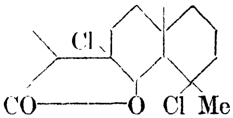
[78] L. Ruzicka, D. R. Koolhaas, and A. H. Wind, *Helv. Chim. Acta*, 1931, **14**, 1171; *A.*, 1931, 1302.



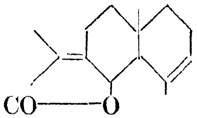
(XV.)



(XVI.)



(XVII.)

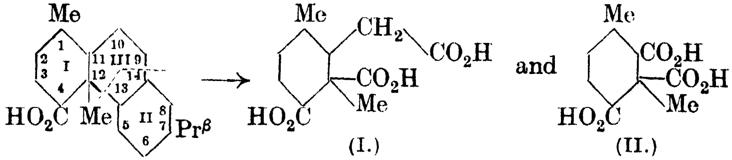


(XVIII.) Alantolactone

Hansen [77] favours the formula (XIV) for the *iso*-lactone; should this prove to be correct, the formula (XVIII) for alantolactone would also require revision, since both (XIV) and (XVIII) would give rise to the same dihydrochloride.

The Resin Acids (continued from *Ann. Reports*, 1927, **24**, 124).—Considerable progress has been made in the elucidation of the structure of abietic and dextropimaric acids and the formulæ assigned to them have attained some degree of certainty.

The new facts are as follows: oxidation of either acid with a large excess of permanganate leads to two acids, $C_{11}H_{16}O_6$ and $C_{12}H_{18}O_6$.[79] The former is dehydrogenated by selenium to *m*-xylene, and the latter to 1 : 2 : 3-trimethylbenzene.[80] In these acids ring I of the parent acids is intact and it can be concluded that the methyl group which is lost in the dehydrogenation of abietic acid to retene occupies position 12, not 11 as hitherto supposed:



(I.) (II.)

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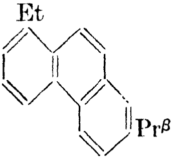
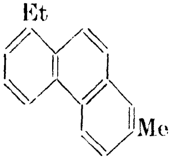
[79] L. Ruzicka, J. Meyer, and M. Pfeiffer, *Helv. Chim. Acta*, 1925, **8**, 637; *A.*, 1925, i, 1419; P. Levy, *Ber.*, 1929, **62**, 2497; A., 1929, 1448.

[80] L. Ruzicka, M. W. Goldberg, H. W. Huyser, and C. F. Seidel, *Helv. Chim. Acta*, 1931, **14**, 545; *A.*, 1931, 736.

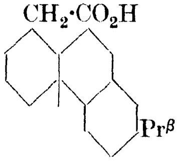
Later work showed that these formulæ required revision and incidentally supplied the final proof of the position of the carboxyl in abietic and dextropimaric acids. F. Vocke [81] found that the C_{11} acid has two carboxyls attached to tertiary carbon atoms, and the same conclusion was independently reached by L. Ruzicka, G. B. R. de Graaff, and H. J. Müller.[82] It had previously been found that methylabietin, in which a methyl group replaces the carboxyl, is dehydrogenated to a methylretene, and methylpimarin, similarly derived from dextropimaric acid, yields a methylpimanthrene.[83] It has now been found [82] that these compounds are oxidised to the same phenanthrene-1 : 7-dicarboxylic acid and that they are therefore homoretene (III) and homopimanthrene (IV) respectively :



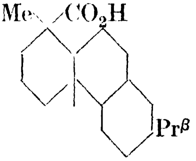
(III.)



(IV.)

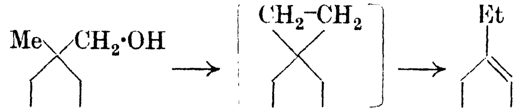


(V.)



(VI.)

This means either that the carboxyl in the resin acids is attached to a methyl group as in (V) or that both groups are attached to the nucleus in position 1 as in (VI). The former alternative is contrary to the " isoprene rule " and does not account for the difficult esterification of these acids, which is adequately expressed by formula (VI). The formation of an ethyl group in the dehydration of abietinol is doubtless due to a pinacolic change :



The same conclusion was independently reached by R. D. Haworth,[85] who, in addition, synthesised homoretene and homopimanthrene and placed their structure beyond all doubt.

The skeleton of abietic acid is thus finally settled. The acid and its ester combine with maleic anhydride [86] and therefore contain a system of conjugated double bonds, the possible positions of which are represented in formula (VII) by thick lines; of these, the

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[81] *Annalen*, 1932, **497**, 247; *A.*, 1036.

[82] *Helv. Chim. Acta*, 1932, **15**, 1300; *A.*, 1254.

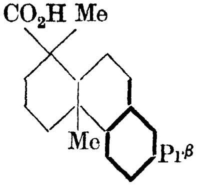
[83] *Ann. Reports*, 1927, *loc. cit.*

[85] *J.*, 1932, 2717.

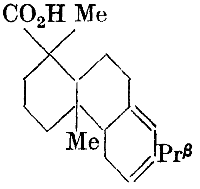
[86] L. Ruzicka, P. J. Ankersmit, and B. Frank, *Helv. Chim. Acta*, 1932, **15**, 1289; *A.*, 1254.

9 : 14-position is considered to be excluded for steric reasons and the arrangement (VIII) is the most likely :

(VII.)

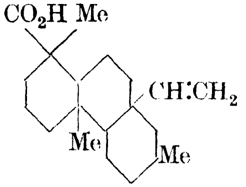


(VIII.)

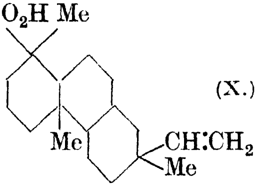


Dextropimaric acid does not form an addition product with maleic anhydride and therefore does not contain a system of conjugated double bonds. On oxidation with excess of permanganate it gives the same two acids (I) and (II), and therefore has the same substituents in ring I, as abietic acid;[87] on ozonisation it gives formaldehyde, proving the presence of a terminal CH_2 group. The following formulæ are therefore considered likely :

(IX.)

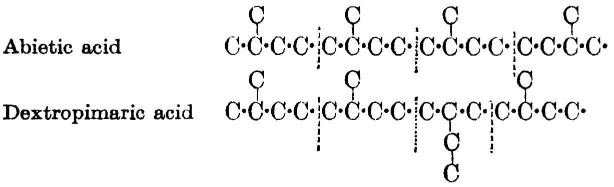


(X.)



Of these, (IX) is much the more probable because tetrahydrodextropimaric acid is dehydrated by selenium to pimanthrene, as would be expected; from a compound of the alternative structure, some 1-methyl-7-ethylphenanthrene should be formed.

The suggested formulæ for abietic and dextropimaric acids are derived from irregular isoprene chains :



$$\text{Abietic acid}\quad C{\cdot}\overset{C}{C}{\cdot}C{\cdot}C{\cdot}\,\vdots\,C{\cdot}\overset{C}{C}{\cdot}C{\cdot}C{\cdot}\,\vdots\,C{\cdot}\overset{C}{C}{\cdot}C{\cdot}C{\cdot}\,\vdots\,C{\cdot}\overset{C}{C}{\cdot}C{\cdot}C{\cdot}$$

$$\text{Dextropimaric acid}\quad C{\cdot}\overset{C}{C}{\cdot}C{\cdot}C{\cdot}\,\vdots\,C{\cdot}\overset{C}{C}{\cdot}C{\cdot}C{\cdot}\,\vdots\,C{\cdot}\underset{\underset{C}{C}}{C}{\cdot}C{\cdot}\,\vdots\,C{\cdot}\overset{C}{C}{\cdot}C{\cdot}C{\cdot}$$

Agathic (more strictly, agathicdicarboxylic) acid, $C_{20}H_{30}O_4$ (XI), present in manila or kauri copal, contains two rings and two double bonds[88] and gives on dehydrogenation with selenium 1 : 2 : 5-trimethylnaphthalene and a hydrocarbon $C_{17}H_{20}$ (XII). On treatment with formic acid a further ring is closed, forming *iso*agathic acid

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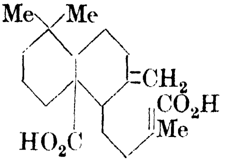
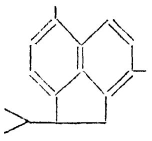
[87] L. Ruzicka, G. B. R. de Graaff, M. W. Goldberg, and B. Frank, *Helv. Chim. Acta*, 1932, **15**, 915; *A.*, 948; R. D. Haworth, *loc. cit.*

[88] L. Ruzicka and J. R. Hosking, *Annalen*, 1929, **469**, 572; *A.*, 1929, 572.

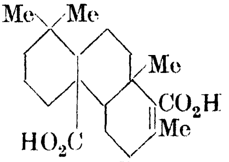
(XIII),[89] which contains one double bond and is dehydrogenated to pimanthrene; a small amount of the latter is also produced from agathic acid itself.



(XI.)



(XII.)

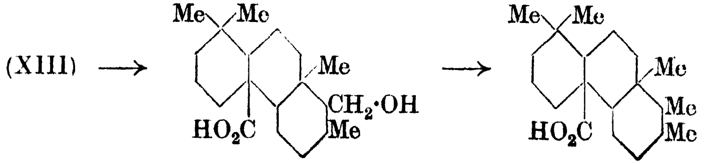


(XIII.)

One carboxyl group is lost by agathic and *iso*agathic acid on melting, noragathic and nor*iso*agathic acid respectively being formed. One ester group in methyl agathate is readily hydrolysed and the free carboxyl also is easily split off, leading to methyl noragathate; the latter is only hydrolysed with extreme difficulty, and the same applies also to the second ester group in methyl agathate and to both ester groups in methyl *iso*agathate. The first carboxyl is therefore probably situated next to a double bond in the side chain, on a carbon atom which is involved in the conversion of agathic acid into the *iso*-acid, since the character of this carboxyl changes completely on cyclisation of the acid. The same double bond is also the only one to be reduced by sodium and alcohol and if it is αβ to the carboxyl, it is probable that there are no other substituents in the vicinity. The results of ozonisation, which gives formaldehyde, formic and oxalic acids, also support this formulation and confirm the presence of the terminal CH_2 group in agathic acid.

The second carboxyl must occupy a sterically protected position, being quite different from the carboxyl in abietic or dextropimaric acid; and on the assumption that the acid is derived from a regular arrangement of isoprene units, the position 12 for this group is to be preferred to the alternative one, 11.

Moreover, one carbomethoxyl group of methyl *iso*agathate can be reduced, though not so easily as that in methyl agathate; the carbinol group is then converted into methyl, and the product on dehydrogenation with selenium passes into a new trimethylphenanthrene. This shows that the carboxyl which is not reduced occupies a different position from that in abietic acid:



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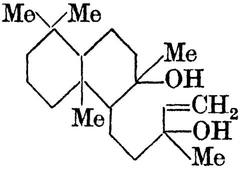
[89] L. Ruzicka and J. R. Hosking, *Helv. Chim. Acta*, 1930, **13**, 1402; 1931, **14**, 203; *A.*, 1931, 231, 359.

The diterpenic alcohol sclareol, from the oil of *Salvia sclarea*, appears to be closely connected with agathic acid. It is a ditertiary alcohol with a terminal CH_2 group oxidisable to formåldehyde, converted into 1 : 2 : 5-trimethylnaphthalene on dehydrogenation. The probable formula (XIV) is put forward for it.[90]

(XIV.)



A considerable amount of work has lately been carried out on elemic acid, a triterpene derivative, and the related amyrins and sapogenins but the results are not yet ripe for summarising; most authorities, however, now agree that the sapogenins are triterpene derivatives with a C_{30} formula.

Polycyclic Hydrocarbons.

Apart from the technical importance of a number of the more complex hydrocarbons of this group, increasing attention has lately been devoted to the possibility of determining the fine structure of these compounds; the results indicate that speculation has progressed beyond mere guesswork and give a logical explanation of otherwise obscure differences between closely related compounds, such as the great difference in *meso*-reactivity between phenanthrene and anthracene or, better still, *lin.*-benzanthracene, which does not immediately follow from their formulæ. A sensitive test of such reactivity is the reaction of these compounds with maleic anhydride [91] or benzoquinone; [92] thus, phenanthrene does not add the former reagent, whereas anthracene does so readily.[93] The absorption spectra provide another means of investigation and numerous measurements of extinction coefficients have been made; the results of these physical measurements are in good agreement with those of purely chemical investigations.

E. Clar's basic assumption is that these hydrocarbons exhibit valency tautomerism[94] leading to two or more forms, which in anthracene, for example, are (I) and (II):

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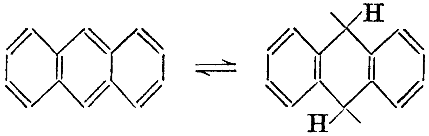
[90] M. M. Janot, *Compt. rend.*, 1930, **191**, 847; 1931, **192**, 845; *A.*, 1931, 94, 737.

[91] O. Diels and K. Alder, *Annalen*, 1931, **486**, 191; *A.*, 1931, 848; E. Clar, *Ber.*, 1931, **64**, [*B*], 2194; *A.*, 1931, 1292.

[92] E. Clar and F. John, *ibid.*, 1930, **63**, [*B*], 2967; E. Clar, *ibid.*, 1931, **64**, [*B*], 1676; *A.*, 1931, 209, 1044.

[93] E. Clar, *ibid.*, 1932, **65**, [*B*], 1425; *A.*, 1131.

(I.)



(II.)

o-quinonoid form diradical form

The second form, referred to as the "R" state, has unshared electrons on the *meso*-carbon atoms and is responsible for the reactivity of these positions, which varies according to the permanence of this phase in different compounds.[95] It is also responsible for the characteristic anthracene absorption bands in the long-wave region of the spectrum.

The catalytic hydrogenation of anthracene, which has lately been re-examined,[96] is readily interpreted in the light of this conception: *e.g.*, the formation of the 9 : 10-dihydride is not an intermediate step in, but takes place concurrently with, the formation of the 1 : 2 : 3 : 4-tetra- and the 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octa-hydride. The dihydride, being a true benzene derivative, is much more slowly hydrogenated than anthracene itself, and similarly the octahydride is only slowly attacked. The dihydride is presumably derived from the "R" state, whereas the quinonoid form is directly hydrogenated to the higher hydrides, without passing through the dihydride as postulated by G. Schroeter.[97] *

The degree of mobility of the unshared electrons in the "R" phase varies with the valency demand of the arylene residues fused to the *meso*-ring and with it the depth of colour of the substance. For instance, 2 : 3-benzanthracene (III), which is more reactive than anthracene, is orange and is photochemically oxidised to the quinone when its xylene solution is shaken with air; and 2 : 3 : 6 : 7-dibenzanthracene (IV) is deep blue,[98] forms a bimolecular peroxide on photochemical oxidation, and instantaneously reacts with maleic anhydride. This indicates that it exists solely in the "R" state and it is actually termed 2 : 3 : 6 : 7-dibenzanthracene-9 : 10-diyl; in agreement with this, its blue solutions do not darken further on heating, an effect observed in some anthracene derivatives,[99] and dissociation is evidently complete.

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[94] E. Clar and F. John, *loc. cit.*

[95] E. Clar, *Ber.*, 1932, **65**, [*B*], 503; *A.*, 608.

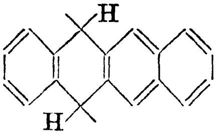
[96] K. Fries and K. Schilling, *ibid.*, p. 1494; *A.*, 1123.

[97] *Ibid.*, 1924, **57**, 2003; *A.*, 1925, i, 127.

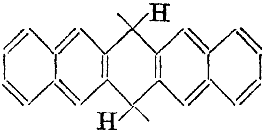
[98] E. Clar and F. John, *ibid.*, 1930, **63**, [*B*], 2967; *A.*, 1931, 209.

* The formation of the tetrahydride from the dihydride, which has been established by Schroeter, may proceed through the intermediate dehydrogenation to anthracene, which has been isolated from the hydrogenation product of the dihydride.

(III.)

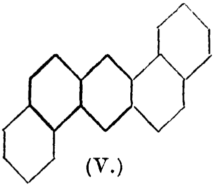


("R" phase alone shown.)

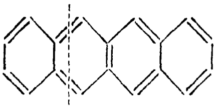


(IV.)

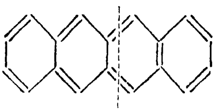
On the other hand, 1 : 2 : 5 : 6-dibenzanthracene (V) reacts slowly with maleic anhydride and is colourless; it is a curious fact that its carcinogenic activity is apparently not directly connected with its chemical reactivity : [1]



(V.)



(VI.)



(VII.)

Now these hydrocarbons can be considered to be derived from quinones; thus, anthracene and 2 : 3-benzanthracene, in its symmetrical form (VI), both embody the skeleton of *o*-benzoquinone. Clar suggests that there is a simple relationship between the reduction potentials of the quinones and the extinction curves of the related hydrocarbons. A number of these potentials have been determined by L. F. Fieser and his collaborators; [2] when plotted against log $\varepsilon_{\text{max.}}$ of the corresponding hydrocarbons, they give a straight line, and thus the reduction potential of an unknown quinone can be predicted if the absorption spectrum of the relevant hydrocarbon is known. Hydrocarbons related to a quinone with a low reduction potential have a short "R" phase and exhibit diminished *meso*-reactivity and *vice versa*; and the corresponding effect is observed in the displacement of the "A" absorption bands of the spectrum.

2 : 3-Benzanthracene in its unsymmetrical form (VII) is derived from the (presumably highly reactive) unknown 2 : 3-naphthaquinone. Similarly, 2 : 3 : 6 : 7-dibenzanthracene can be derived from the latter or from the likewise unstable 2 : 3-anthraquinone; owing to the instability of these quinonoid forms the compound tends to exist more and more in the free radical or "R" state, until in the limiting case of the 2 : 3 : 6 : 7-compound this becomes the only stable condition.

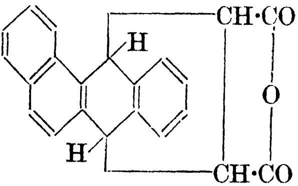
[99] C. K. Ingold and P. G. Marshall, *J.*, 1926, 3080; *A.*, 1927, 141.

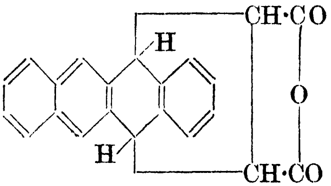
[1] J. W. Cook, *J.*, 1931, 3273; *A.*, 153.

[2] *J. Amer. Chem. Soc.*, 1924, **46**, 1864; 1929, **51**, 3101; 1930, **52**, 5204; *A.*, 1924, ii, 839; 1929, 1452; 1931, 173.

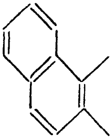
All the extinction curves show, in addition to the " A " bands, an intense band of clearly benzenoid character, though somewhat displaced. The maleic anhydride addition product of anthracene shows a typical benzene spectrum, although it is displaced in the same way, but the corresponding compound from 1 : 2-benzanthracene (VIII) is a typical naphthalene derivative. The free hydrocarbon also shows some characteristics of the naphthalene spectrum, but no trace of this is seen in 2 : 3-benz- and 2 : 3 : 6 : 7-dibenzanthracene, although it reappears in their addition products with maleic anhydride. It is clear that in the latter the effect of the unshared electrons due to the " R " state is no longer observed and the spectrum is entirely due to the benzene (or naphthalene) rings at the side :

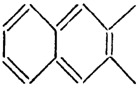
(VIII.)





It can be concluded that the naphthylene residues must have a different structure in *ang.*- and *lin.*-hydrocarbons derived from anthracene; in the former it is symmetrical and in the latter unsymmetrical :





It also follows that the *lin.* attachment of rings to anthracene stabilises the diradical state, whereas the aromatic state is favoured by their *ang.* attachment, which causes a general diminution of reactivity and increase in stability. In accord with this is the observation [3] that the stability of dihydro-derivatives of these compounds goes hand in hand with their increasing *meso*-reactivity. A similar parallelism has already been recorded in the benzonaphthazines.[4]

Phenanthrene has clearly a less pronounced " R " phase than anthracene [5] and is therefore less reactive in the *meso*-positions; at the same time the 1 : 4-positions display a certain reactivity, *e.g.*, towards lithium,[6] and a second diradical phase (XI) may have to be taken into consideration :

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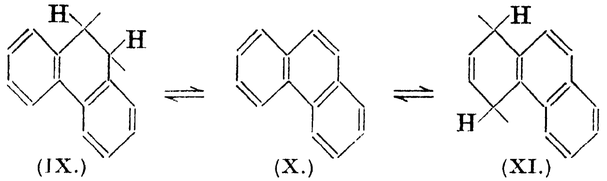
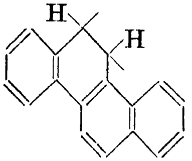
[3] L. F. Fieser, *J. Amer. Chem. Soc.*, 1931, **53**, 2329; *A.*, 1931, 1064.

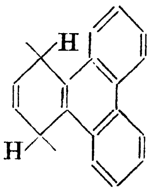
[4] O. Hinsberg, *Annalen*, 1901, **319**, 264; *A.*, 1902, i, 238.

[5] E. Clar and L. Lombardi, *Ber.*, 1932, **65**, [*B*], 1411; *A.*, 1123.

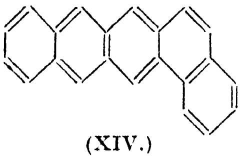

(IX.) (X.) (XI.)

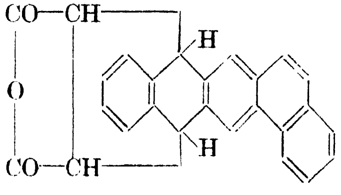
The structure (XI), like (X), is that of a naphthalene derivative, and this is distinctly shown in the extinction curve of the hydrocarbon, in addition to the intense benzene band already noted in the anthracene spectrum. Chrysene (XII) evidently has a similar structure but with a longer 9 : 10-diyl phase. Triphenylene shows a naphthalene-like spectrum ; its diradical phase is evidently the 1 : 4-diyl (XIII) :

(XII.)



(XIII.)

On the other hand, the curve of 2′ : 3′-naphtha-2 : 3-phenanthrene (XIV), a deep orange, highly reactive substance, shows no vestige of phenanthrene character ; it is just like that of 2 : 3-benzanthracene, but reverts to the phenanthrene type when (XIV) combines with maleic anhydride.


(XIV.)



On the assumption that naphthalene has an unsymmetrical structure derivable from that of *o*-benzoquinone, chrysene, phenanthrene, and triphenylene could be respectively linked up with 1 : 2-phenanthraquinone, 1 : 2-naphthaquinone, and 9 : 10-phenanthraquinone ; the reduction potentials of these quinones [7] are not simply related to the log $\varepsilon_{max.}$ as in the anthracenes and it is concluded that in all hydrocarbons formed from naphthalene by *ang.* attachment of phenylene residues there is a double bond between any two rings; this explains the inability of these hydrocarbons to react with maleic anhydride.

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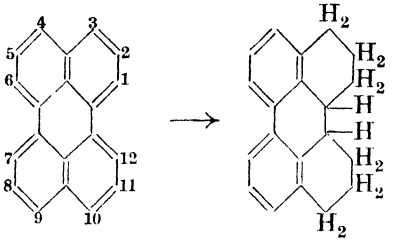
[6] W. Schlenk and E. Bergmann, *Annalen*, 1928, **463**, 84; *A.*, 1928, 1031.

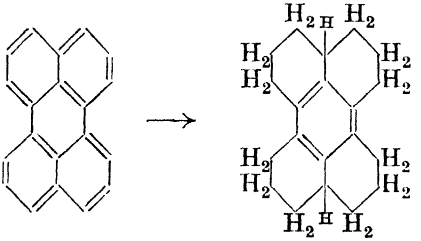
[7] L. F. Fieser and M. A. Peters, *J. Amer. Chem. Soc.*, 1931, **53**, 793; *A.*, 1931, 489.

Perylene presents special interest, being the basis of an important group of colouring matters, and has been the subject of repeated investigation. It is reduced by sodium in amyl alcohol,[8] giving simultaneously an octahydro- and a tetradecahydro-compound, (XVI) and (XVIII); the first is formed in the same way as tetralin from naphthalene, and the formation of the second is like the hydrogenation of anthracene. It is suggested that the isomeric forms of the hydrocarbon (XV) and (XVII) give rise to these reduction products, just as two quinones, the 3 : 9- and the 3 : 10-, are formed on oxidation :

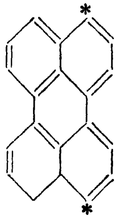
(XV.)



(XVI.)



(XVII.) (XVIII.)



(XIX.)

E. Clar [9] regards formula (XV) as improbable, because the middle ring is triquinonoid and, although the positions 6 : 7 and 1 : 12 are exactly equivalent, perylene reacts with only *one* molecule of maleic anhydride : this and the preferential formation of the 3 : 9-quinone are only explained by the formula (XIX), which is also supported by spectrographic evidence. Thus (XV) contains two naphthalene residues which should find expression in the extinction curve and this is not observed; also, the spectrum of the 2 : 3 : 10 : 11-dibenzo-compound (XX) is very similar to that of the parent hydrocarbon, whereas the addition of two rings to the structure (XV) should cause a marked alteration, similar to that observed on passing from naphthalene to phenanthrene. On the other hand, the curve of the 1 : 12-benzo-compound (XXI), though still of the perylene type, is less intense and evidently corresponds to a more saturated structure; the bands are displaced towards the ultra-violet, doubtless owing to the inclusion of the double bonds of the quinonoid system in the new benzene ring.

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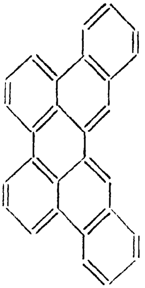
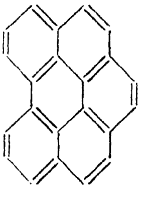
[8] A. Zinke and O. Benndorf, *Monatsh.*, 1932, **59**, 241; *A.*, 507.

[9] *Ber.*, 1932, **65**, [*B*], 846; *A.*, 731.

(XX.)

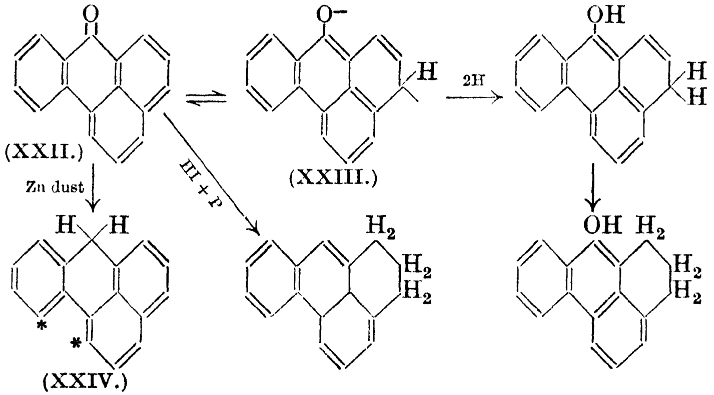




(XXI.)

The anthraquinonoid formula (XVII), however, accounts for some of the reactions of perylene and is retained; the distinctive character of perylene is attributed to the conjugated system 3 : 10 (marked with asterisks in formula XIX).

Benzanthrone is easily reduced, taking up four atoms of hydrogen,[10] and behaves towards the Grignard reagent as an unsaturated ketone.[9] This behaviour is held to indicate that an equilibrium exists between the forms (XXII) and (XXIII):



(XXII.) (XXIII.) (XXIV.)

Benzanthrene (XXIV), formed by replacing the carbonyl group of benzanthrone by a methylene group, gives a typical *naphthalene* spectrum as would be expected from the above, but not from the alternative, anthracene-like, formulation; its reactivity, *e.g.*, with maleic anhydride, is due to the conjugated system marked by asterisks (compare perylene). This arrangement is not present in benzanthrone, which, like phenanthrene and chrysene, does not form an addition product. These differences in reactivity are inexplicable on the basis of such formulæ as J. J. Thomson's (Rădulescu's formula, XXVI) and give strong support for a formulation with actual double bonds disposed in a definite manner.[11]

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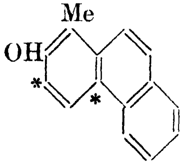
[10] J. v. Braun and O. Bayer, *Ber.*, 1925, **58**, 2667; *A.*, 1926, 172.

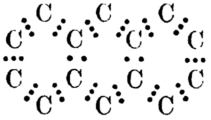
Recent experiments suggest that the electromeric phases in polycyclic compounds can have considerable stability;[12] *e.g.*, 2-retenol (XXV) does not couple with diazotised amines. The addition of the latter would normally occur either at a double bond or at the end of a conjugated system (*i.e.*, ortho or para to the hydroxyl), but neither of these alternatives (marked by asterisks) is available and no coupling occurs :

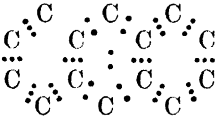


(XXV.)

D. Rădulescu and his collaborators[13] have measured the extinction curves of a number of organic compounds, including anthracene, phenanthrene, pyrene, perylene, and 2 : 3-benzanthracene, and interpreted them in the light of his theoretical views, which cannot be conveniently summarised. He also assumes valency tautomerism in polycyclic hydrocarbons and his conclusions, based on spectrographic work, are similar to Clar's. His formulæ are, however, different; those adopted for anthracene, for example, are (XXVI) and (XXVII); the latter thus corresponds to a para-bridged phase, and the former is J. J. Thomson's original electronic formula :

(XXVI.)





(XXVII.)

The spectral bands due to the bridged phase are the " A " bands in the long-wave region attributed by Clar to the " R " phase. The essential difference, therefore, between these formulæ is that in the bridged one the odd electrons are controlled by *both meso*-carbons, whereas in the diradical formula they are unshared. E. Clar and many others are strongly opposed to the bridged formulation, which in any case cannot account for the behaviour of compounds such as 2 : 3 : 6 : 7-dibenzanthracene-9 : 10-diyl, the diradical nature of which appears to be beyond dispute, and it seems to the Reporter that, even if the existence of a bridged phase is admitted, this cannot supersede the diradical phase. The *limiting* phases required to account for the facts are the quinonoid and the diradical.

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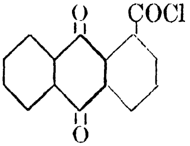
[11] E. Clar, *Ber.*, 1932, [*B*], **65**, 1425; *A.*, 1131.

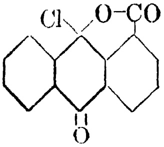
[12] L. F. Fieser and M. N. Young, *J. Amer. Chem. Soc.*, 1931, **53**, 4120; *A.*, 163. The experiments of A. A. Levine and A. G. Cole (*ibid.*, 1932, **54**, 338; *A.*, 259) on the ozonisation of *o*-xylene prove the separate existence of the two Kekulé individuals.

[13] *Ber.*, 1931, **64**, [*B*], 2223 *et seq.*; *A.*, 1931, 1351.

The synthesis of coronene (hexabenzobenzene) by R. Scholl and K. Meyer [14] was made possible by the discovery [15] that the chlorides of anthraquinone-1-carboxylic acids react in two tautomeric forms (I) and (II), in both of which the chlorine can be replaced by an aromatic residue by the Friedel–Crafts reaction.

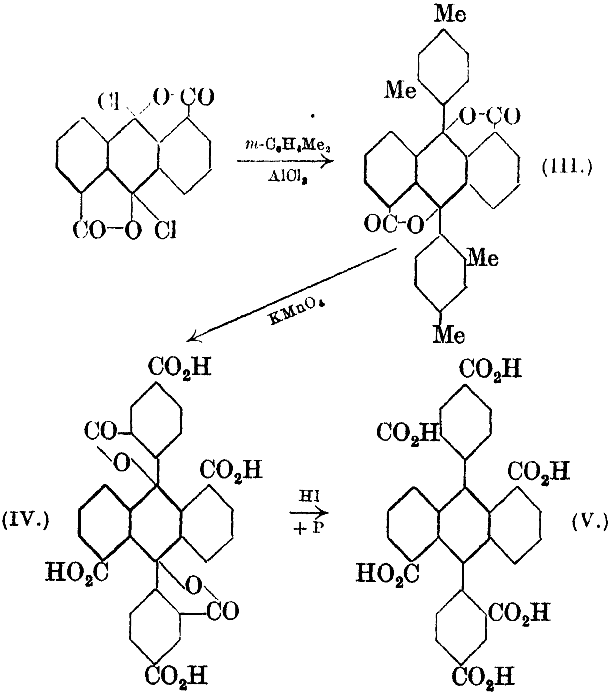
(I.)





(II.)

Thus the chloride of anthraquinone-1 : 5-dicarboxylic acid condenses with *m*-xylene, giving mainly the compound (III); this is oxidised by permanganate to the lactonic acid (IV), which is reduced with hydriodic acid and phosphorus to the hexacarboxylic acid (V):



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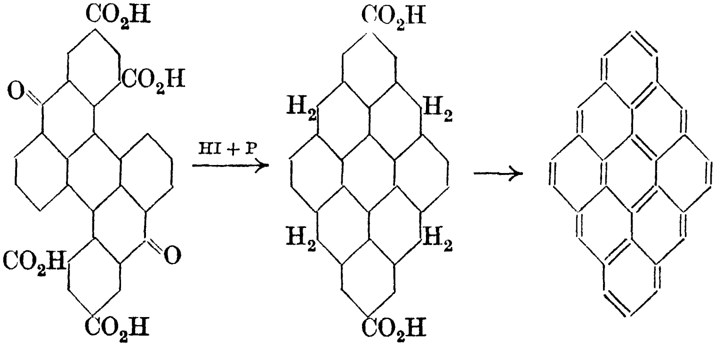
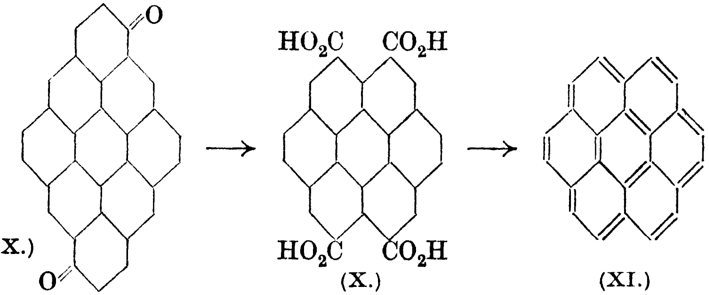
[14] *Ber.*, 1932, **65**, [*B*], 902; *A.*, 731.

[15] R. Scholl, H. Dehnert, and L. Wanka, *Annalen*, 1932, **493**, 56; R. Scholl, H. K. Meyer, and W. Winkler, *ibid.*, **494**, 201; *A.*, 274, 617.

The acid (V) can undergo ring closure in several different ways: 20% oleum produces the compound (VI), which can be reduced with further ring closure to the acid (VII), from which, by heating with soda-lime and copper powder, dibenzocoronene (VIII) is obtained. This, treated with dilute nitric passes through a red diquinone (IX), giving a blue vat, into the acid (X), which is decarboxylated with soda-lime to coronene itself (XI).



(VI.) (VII.) (VIII.)

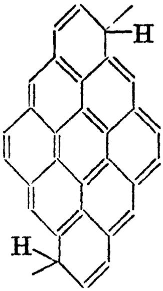


(IX.) (X.) (XI.)

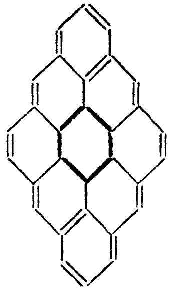
The hydrocarbon is pale yellow with a blue fluorescence, high-melting, and extremely stable. These properties are best expressed by the formula (XI), in which the central ring is a true benzene ring and the double bonds in the peripheral ring system form a continuous conjugated system.

The dibenzo-compound (VIII) forms a complete contrast to coronene; it is highly coloured, and its red solutions have a green fluorescence and are readily oxidised in the air; it is readily converted into the quinone (IX) and gives a dark blue dibromide (probably a carbonium salt). Such reactivity suggests a diradical structure (XII); the authors, however, prefer the alternative structure (VIII), which in their opinion suffices to explain the behaviour of the substance. They also suggest electronic formulæ (XIII) and (XIV) for dibenzocoronene and coronene, in which the thick lines represent three-electron linkages and the fine lines two-electron linkages.

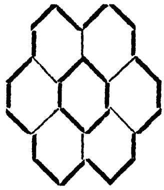
These are open to the same objections as the non-committal formulæ discussed on p. 170.



(XII.)



(XIII.)



(XIV.)

The Reporter wishes to thank Dr. J. W. Cook for many helpful suggestions.

Rubrenes.

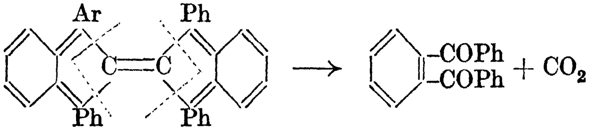
No account has yet been given in these Reports of a remarkable group of substances discovered in 1926.[16]

Rubrene, the type of the series, is a red hydrocarbon, $C_{42}H_{28}$, dissolving in benzene with a yellow fluorescence, and is prepared by heating the chloride (I) :

$$\text{(I.)} \quad 2Ph_2CCl{\cdot}C{:}CPh = C_{42}H_{28} + 2HCl$$

On oxidation with chromic acid [17] rubrene gives *o*-dibenzoylbenzene and carbon dioxide, in accordance with the structure (II; Ar = Ph) assigned to it.[18]

(II.)



The dibenzofulvene formula (II) accounts satisfactorily for the colour and fluorescence of rubrene and its mode of formation. The mechanism suggested for the latter as the most likely [18] involves, first of all, the migration of the chlorine from the α- to the γ-carbon atom of the acetylenic compound, a process analogous to the migration of the hydroxyl group in the corresponding carbinol [19] (III), which readily passes into the ketone (IV) :

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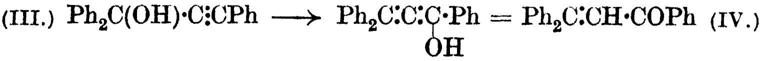
[16] C. Moureu, C. Dufraisse, and P. M. Dean, *Compt. rend.*, 1926, **182**, 1440; *A.*, 1926, 945.

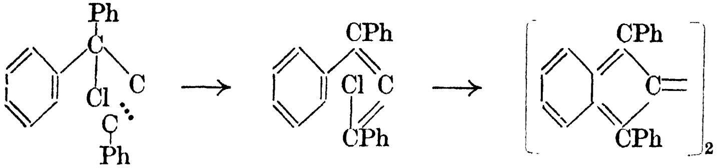
[17] C. Moureu, C. Dufraisse, and L. Enderlin, *ibid.*, 1928, **187**, 406; *A.*, 1928, 1127; C. Dufraisse and L. Enderlin, *Bull. Soc. chim.*, 1932, [iv], **51**, 132; *A.*, 507.

[18] A. Willemart, *Compt. rend.*, 1928, **187**, 385; *A.*, 996; *Ann. Chim.*, 1929, [x], **12**, 345; *A.*, 1930, 334.

[19] K. H. Meyer and K. Schuster, *Ber.*, 1922, **55**, 819; *A.*, 1922, i, 556.

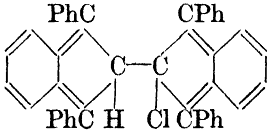


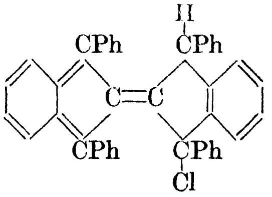
$$\text{(III.)}\ Ph_2C(OH){\cdot}C{\vdots}CPh \longrightarrow Ph_2C{:}C{:}\underset{OH}{C}{\cdot}Ph = Ph_2C{:}CH{\cdot}COPh\ \text{(IV.)}$$



J. Robin[20] has made a further study of the formation of rubrene. He finds that the chloride (I) passes on keeping or on treatment with ammonia or an aliphatic amine into a compound still containing halogen, evidently formed by loss of one molecule of hydrogen chloride from two of the acetylenic compound. The new compound passes easily and quantitatively into rubrene and is formulated as a hydrochloride such as (V) or (VI):

(V.)

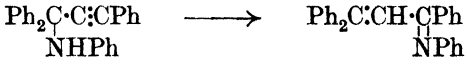




(VI.)

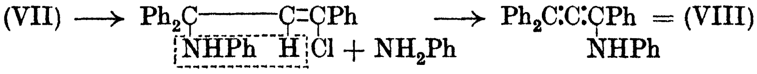
the corresponding hydroxy- and ethoxy-compound have also been obtained.

With aniline (and other primary arylamines) the chloride (I) forms a colourless (VII) and a yellow (VIII) nitrogenous derivative; the former is converted into the latter when heated with aniline hydrochloride, and its hydrochloride undergoes the same change, especially in aniline solution.



$$\text{(VII.)}\ Ph_2\underset{NHPh}{C}{\cdot}C{\vdots}CPh \longrightarrow Ph_2C{:}CH{\cdot}\underset{NPh}{\overset{}{C}}Ph\ \text{(VIII.)}$$

(VIII) can be hydrolysed to the ketone (IV) and its constitution is thus proved. The change therefore provides an interesting example of tautomeric change similar to that observed by Meyer and Schuster.[19] Robin prefers to formulate it as involving the addition of hydrogen chloride, which is then eliminated as aniline hydrochloride, on the ground that hydrogen chloride is indispensable for this transformation:



$$\text{(VII)} \longrightarrow Ph_2\underset{\boxed{NHPh\quad H}}{C}\text{———}\underset{H}{C}{=}\underset{Cl}{C}Ph + NH_2Ph \longrightarrow Ph_2C{:}C{:}\underset{NHPh}{C}Ph = \text{(VIII)}$$

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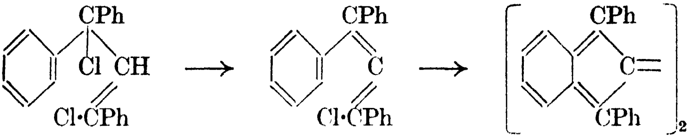
[20] *Ann. Chim.*, 1931, [x], **16**, 421; *A.*, 1932, 260; compare C. Moureu, C. Dufraisse, and J. Robin, *Compt. rend.*, 1929, **188**, 1582; *A.*, 1929, 922.

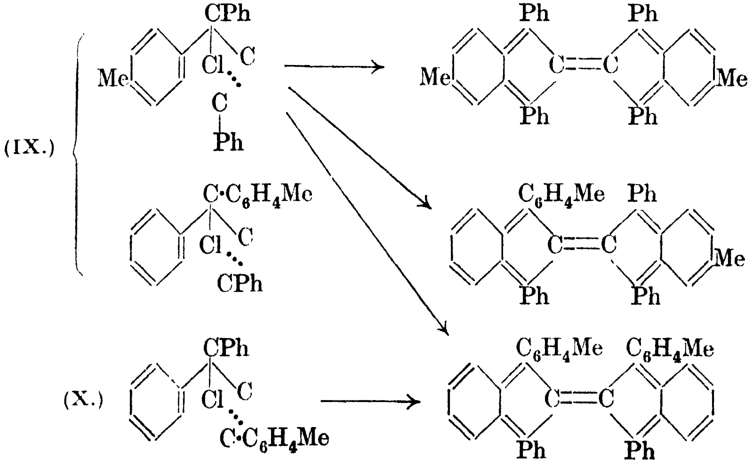
Similarly, he assumes the intermediate addition of hydrogen chloride to the chloride (I) in the conversion of the latter into rubrene :



The cyclisation of the compound may take place either before or after the elimination of hydrogen chloride.

This view of the process is, like all similar theories, difficult to disprove, but nevertheless appears to be superfluous when account is taken of the proved occurrence of tautomeric changes in similarly constituted ethylenic systems; in addition, Meyer and Schuster[19] have shown that the analogous transformation of the corresponding carbinol cannot be due to the addition and elimination of water, since it proceeds most readily in the presence of strong dehydrating agents (acetic anhydride) and bears a marked resemblance to the changes subsequently examined by Burton and Ingold.[21]

The early experiments indicated that only chlorides of the type $Ph_2CCl{\cdot}C⋮CAr$ gave rise to rubrenes, but unsymmetrical compounds of the type $PhArCCl{\cdot}C⋮CAr$ have since been successfully employed :[22] the former can furnish only one rubrene; a compound such as (IX) can give rise to three different rubrenes, one of which should be identical with that obtained from the isomeric chloride (X). This prediction is verified by experiment and provides good support for the scheme of formation of rubrenes given above.



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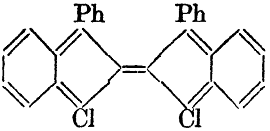
[21] *J.*, 1928, 904; *A.*, 1928, 634; compare *Ann. Reports*, 1928, **25**, 127.

[22] C. Dufraisse and M. Loury, *Compt. rend.*, 1932, **194**, 1664, 1832; *A.*, 732.

C. Dufraisse and R. Buret [23] have prepared a rubrene (XI), in which two of the phenyl residues are replaced by chlorine, from the ketone (XII) by the action of phosphorus pentachloride.



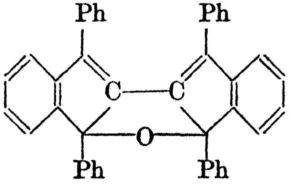
(XI.)

(XII.) $Ph\cdot CO\cdot C\vdots CPh$

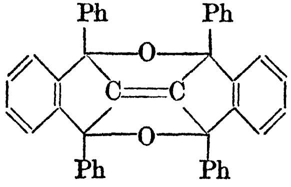
The most remarkable property of the rubrenes is their ability to absorb oxygen on irradiation; no reaction takes place in the dark.[15] A solvent such as benzene is also necessary; no reaction takes place in water or acetic acid, in which rubrene is insoluble,[24] but even a rapidly oxidisable solvent such as benzaldehyde can be employed. " Antioxygens " such as quinol or resorcinol retard the reaction, but their effect is purely chemical and not due to screening.

The completion of the change is marked by the disappearance of colour and especially fluorescence. The product is an oxide, RO_2, crystallising with half a molecule of benzene or other solvent of crystallisation, from which it cannot be freed without decomposition; it has the remarkable property of giving up its oxygen when heated, regenerating the parent hydrocarbon, the change being accompanied by an *emission* of light. Its formation and dissociation can therefore be written : $R + O_2 + \text{light} \rightleftharpoons RO_2$.

This dissociable dioxide, oxyrubrene, is reduced by zinc and acetic acid to a monoxide, metrubrene, which can also be obtained by the mild oxidation of rubrene with permanganate or chromic acid; [25] this can be reduced to rubrene but cannot be oxidised to oxyrubrene. Oxyrubrene is isomerised by the action of a Grignard reagent to *iso*oxyrubrene, which no longer dissociates when heated, but can be reduced to rubrene [26] and therefore contains the same carbon skeleton. The formulæ (XIII) and (XIV) are suggested for these two oxides.



(XIII.) Metrubrene



(XIV.) *iso*Oxyrubrene

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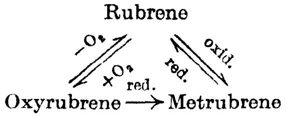
[23] *Compt. rend.*, 1932, **195**, 962.

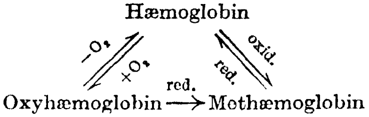
[24] C. Moureu, C. Dufraisse, and C. L. Butler, *ibid.*, 1926, **183**, 101; *A.*, 1926, 945.

[25] C. Moureu, C. Dufraisse, and L. Enderlin, *ibid.*, 1929, **188**, 1528; *A.*, 1929, 922.

[26] C. Dufraisse and M. Badoche, *ibid.*, 1930, **191**, 104; *A.*, 1930, 1173.

The relationship between rubrene, metrubrene, and oxyrubrene is remarkably like that between hæmoglobin and its oxidation products and the names of the compounds are intended to emphasise this similarity :[26]





Such reversible oxidations are unknown except in the respiratory pigments, in which this property has generally been connected with the presence of iron in the molecule. Oxidations are usually accompanied by a considerable liberation of energy and would not be expected to be reversible for that reason.

The heats of formation of rubrene and its oxides are as follows :[27]

Rubrene.	Oxyrubrene.	*iso*Oxyrubrene.	Metrubrene.
– 131	– 108·4	– 50·4	– 92·4

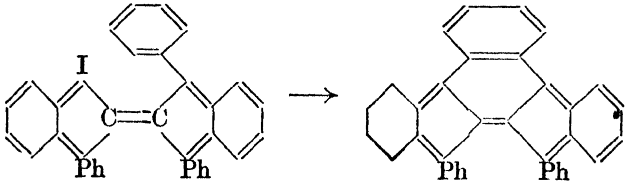
The difference between the heats of formation of rubrene and oxyrubrene (23 cals.) is less than the heat required for the formation of an oxide ring (50 cals.) or a carbonyl group (100 cals.). Nevertheless, the photochemical formation of oxyrubrene is exothermic and the activating action of light can presumably be replaced by some other catalytic influence.

An interesting transformation has been observed as the result of the prolonged action of a Grignard reagent on *iso*oxyrubrene.[28] The product is a magnesium derivative which on treatment with water gives phenol and a rubrene (II; Ar = H) containing one phenyl group less than the initial material; similarly, with iodine, an iodo-rubrene (II; Ar = I) is produced, and with carbon dioxide the corresponding carboxylic acid :

$$C_{42}H_{28}O_2 + 2Mg = C_{36}H_{23}{\cdot}Mg{\cdot}OPh + MgO \longrightarrow PhOH + C_{36}H_{24}.$$

The compound (II; Ar = H) is a typical rubrene, forming a dissociable oxide and having the other characteristic properties of the class.

The iodo-compound (II; Ar = I) on treatment with sodium ethoxide loses hydrogen iodide and forms a violet hydrocarbon (XV), the change probably taking place as follows :[29]



(XV.)

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[27] C. Dufraisse and L. Enderlin, *Compt. rend.*, 1930, **191**, 1321; *A.*, 1931, 171.

[28] C. Dufraisse and M. Badoche, *ibid.*, 1931, **193**, 242; *A.*, 1931, 1151.

[29] *Idem*, *ibid.*, p. 529; *A.*, 1931, 1407.

The intensification of colour is to be expected, since a naphthaquinone group is present in the new compound in addition to the rubrene skeleton, which remains intact.

Sterols and Bile Acids.

The year under review has seen important developments of this subject, discussion of which must be deferred until next year owing to lack of space. A summary of the present position with regard to the bile acids and cholesterol has been published by A. Windaus.[30]

G. A. R. KON.

PART III.—HETEROCYCLIC DIVISION.

HETEROCYCLIC chemistry of to-day is almost synonymous with the chemistry of heterocyclic natural products. The past 50 years have been spent in perfecting the implements with which the organic chemist of to-day works. Discoveries of new methods of wide applicability, such as the remarkable "diene" synthetic and analytic method of O. Diels and K. Alder,[1] must of necessity be few and far between. A new chemistry is, however, arising which has a boundless future before it—chemistry under natural or biological conditions. Already we have some striking examples of its applicability, especially in the field of alkaloidal chemistry.

In 1905 A. Pictet suggested that alkaloids arose from proteins and amino-acids and the view was developed by E. Winterstein and G. Trier,[2] who appear to have been the first to suggest a biogenetic mechanism for the *iso*quinoline group. The thesis was, however, put in an unassailable position by R. Robinson,[3] who illustrated it by syntheses of tropinone [4] and ψ-pelletierine [5] by methods which might occur in the plant and extended it by the synthesis of *N*-methylhomogranatoline [6] and some analogues of ψ-pelletierine.[7]

From Angostura bark, E. Späth and his co-workers isolated and identified a series of quinoline alkaloids which on account of their similarity of structure were thought to arise in the plant from some common parent benzene derivative, probably a derivative of anthranilic acid. This line of thought has been followed up experimentally by C. Schöpf and G. Lehmann,[8] who find that when

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[30] *Z. physiol. Chem.*, 1932, **213**, 147.

[1] *Annalen*, 1932, **498**, 1, 16; *A.*, 1144.

[2] "Die Alkaloide," 1910.

[3] *J.*, 1917, **111**, 876; *A.*, 1917, i, 664.

[4] *Ibid.*, p. 762; *A.*, 1917, i, 581.

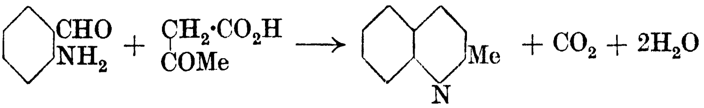
[5] R. C. Menzies and R. Robinson, *J.*, 1924, **125**, 2163; *A.*, 1924, i, 1335.

[6] B. K. Blount and R. Robinson, *J.*, 1932, 1429; *A.*, 759.

[7] *Idem, ibid.*, p. 2485; *A.*, 1147.

[8] *Annalen*, 1932, **497**, 7; *A.*, 1046.

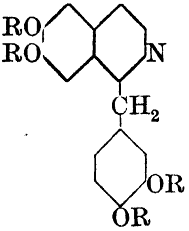
o-aminobenzaldehyde and acetone are brought together in dilute aqueous solution of p_H 3, 5, 7 or 9 no quinaldine is formed but at p_H 12—13 a smooth Friedländer synthesis occurs with formation of quinaldine. If, however, acetone is replaced by acetoacetic acid, a 90% yield of quinaldine may be obtained after 16 days at 25° and p_H 6·8.

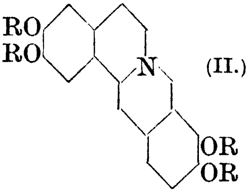


If the reaction is carried out at p_H 13, no loss of carbon dioxide occurs and quinaldine-3-carboxylic acid is formed almost quantitatively. In a similar manner 2-*n*-amylquinoline may be obtained from hexoylacetic acid and *o*-aminobenzaldehyde.

The *iso*quinoline group of alkaloids is exceedingly rich in its variety of examples and no one who surveys the different types can fail to be convinced that they owe their biogenetic origin to the units suggested by Winterstein and Trier. The four main groups are the papaverine group (I), the berberine group (II), the phenanthripyridine group (III), and the morphine group (IV).

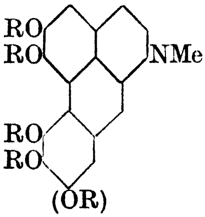
(I.)

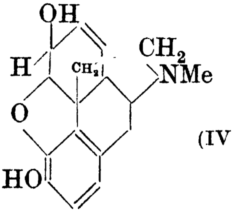




(II.)

(III.)

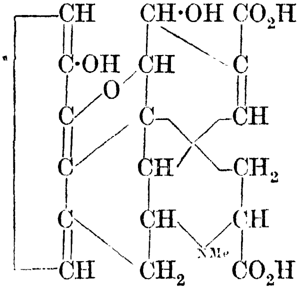


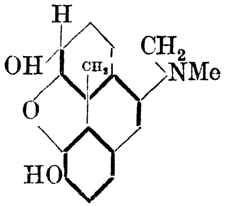


(IV.)

The units in papaverine and the phenanthripyridine group are 3 : 4-dihydroxyphenylethylamine and 3 : 4-dihydroxyphenylacetaldehyde, the latter giving rise to the benzyl portion of the molecule, and in the berberine group the intervention of formaldehyde is also necessary. The morphine group, which includes sinomenine, also contains these two units, although in the case of morphine there is some doubt as to how the ethylamino side-chain arrives on the tertiary carbon atom. One plausible explanation has been given by R. Robinson and S. Sugasawa.[9] Morphine, however, is accompanied in opium by over 22 other alkaloids, the majority of which are clearly framed from the same two units, so there can be no doubt whatever that morphine has a similar biogenetic origin. It is therefore surprising to find that H. Emde [10] regards morphine as having arisen from three molecules of a hexose and one of methylamine with loss of carbon dioxide and water, and to visualise this he postulates a pro-morphine (V) in the plant, which loses carbon dioxide. The two intact hexose chains seen in (V) are shown in (VI) in bolder print and it will be at once clear that the scheme, whilst ingenious, fails to carry conviction.

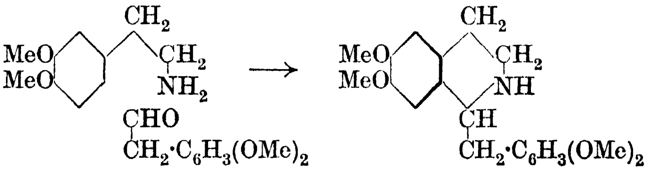
(V.)





(VI.)

A synthesis of an *iso*quinoline alkaloid under biological conditions has not yet been effected, although a synthesis of tetrahydropapaverine in 8% yield from homoveratraldehyde and homoveratrylamine in the presence of 19% hydrochloric acid and at a water-bath temperature, based on the Winterstein–Trier mechanism, has been effected by E. Späth and F. Berger.[11]



Stereochemistry.

An interesting example of spiro-asymmetry has been recorded by (Sir) W. J. Pope and J. B. Whitworth.[12] *spiro*-5 : 5-Dihydantoin (I) has been resolved by crystallisation in alcoholic solution with two molecular proportions of brucine. The behaviour is somewhat novel, for a hot solution of the components deposits a salt of the form 1B,*l*A in an almost pure condition and on allowing the filtrate to stand an almost pure salt of the form 2B,*d*A separates. Evidence has also been obtained pointing to the existence of 3 tautomeric forms (I), (II), and (III), for when the hydantoin (I) with similar

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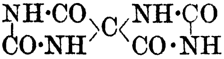
[9] *J.*, 1931, 3163; *A.*, 174. [10] *Naturwiss.*, 1930, **18**, 539; *A.*, 1930, 1072.

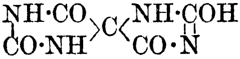
[11] *Ber.*, 1930, **63**, 2098; *A.*, 1930, 1454.

[12] *Proc. Roy. Soc.*, 1931, [*A*], **134**, 357; *A.*, 171.



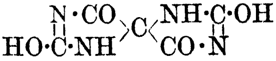
$$\begin{array}{l}\mathrm{NH{\cdot}CO}\\ \mathrm{CO{\cdot}NH}\end{array}\!>\!C\!<\!\begin{array}{l}\mathrm{NH{\cdot}CO}\\ \mathrm{CO{\cdot}NH}\end{array}$$

(I.)



$$\begin{array}{l}\mathrm{NH{\cdot}CO}\\ \mathrm{CO{\cdot}NH}\end{array}\!>\!C\!<\!\begin{array}{l}\mathrm{NH{\cdot}COH}\\ \mathrm{CO{\cdot}N}\end{array}$$

(II.)



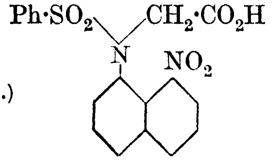
$$\begin{array}{l}\mathrm{N{\cdot}CO}\\ \mathrm{HO{\cdot}C{\cdot}NH}\end{array}\!>\!C\!<\!\begin{array}{l}\mathrm{NH{\cdot}C{\cdot}OH}\\ \mathrm{CO{\cdot}N}\end{array}$$

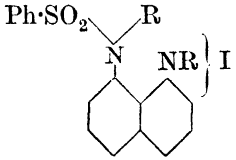
(III.)

rotations in alcohol, water, and pyridine is dissolved in one molecular proportion of sodium hydroxide solution the rotation falls to about one-half its value through formation of the keto-enolic form. When (I) is dissolved in two or more molecular proportions of alkali, the solution is temporarily stable and shows a change of sign of rotation through formation of a di-enolic form. Incidentally the usefulness of brucine for forming salts with hydantoins is thus well established and should lead to the direct resolution of hypnotics of the nirvanol, luminal type, examples of which are hitherto unrecorded.[12a] T. Nishikawa [13] obtained crystalline brucine salts from his α- and β-forms of *C*-methylbarbituric acid, but failed to resolve either, whilst C. M. Hsueh and C. S. Marvel [14] were unable to isolate stable salts of alkaloids with ethyl-*sec*.-butylbarbituric acid.

Another contribution [15] from the Cambridge laboratories fulfils the prediction made in an earlier paper [16] that quaternary salts of 8-substituted derivatives of quinoline should exhibit a molecular dissymmetry which is dependent on restricted rotation about a single bond. Previously it had been shown that benzenesulphonyl-8-nitronaphthylglycine (IV) could be resolved into dextro- and lævo-modifications and now it has been demonstrated that

(IV.)





(V.)

8-benzenesulphonylethylamino-1-ethylquinolinium iodide (V, R = Et) can also exist in optically active forms. In either case the group on the adjacent *peri*- or 1-position restricts the free rotation of the trebly substituted nitrogen atom about the bond linking it to the nucleus.

[12a] See, however, H. Sobotka, M. F. Holzman, and J. Kahn, *J. Amer. Chem. Soc.*, 1932, **54**, 4697.

[13] *Mem. Ryojun Coll. Eng.*, 1931, **3**, 277.

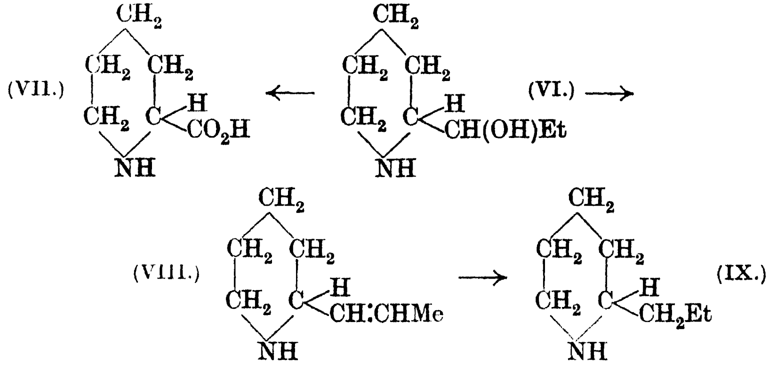
[14] *J. Amer. Chem. Soc.*, 1928, **50**, 855; *A.*, 1928, 529.

[15] W. H. Mills and J. G. Breckenridge, *J.*, 1932, 2209.

[16] W. H. Mills and K. A. C. Elliott, *J.*, 1928, 1291; *A.*, 1928, 748; *Ann. Reports*, 1928, **25**, 117.

The determination of the configuration of optically active substances is an aid to classification, but it often taxes the ingenuity of chemists. There are two methods employed, both of limited application. In the first and more direct method the change of rotation is observed in transformations which do not involve replacements of groups directly attached to the asymmetric carbon atom and where optical inversion is presumably excluded. A classic example is the demonstration by K. Freudenberg[17] that *l*-glyceric acid, *l*-lactic acid, *d*-malic acid, and *d*-tartaric acid all possess the same relative spatial configurations of hydrogen atoms, hydroxyl and carboxyl groups attached to the asymmetric centre. The second method, introduced by G. W. Clough,[18] is a less direct one. It is assumed that "the optical rotatory powers of similarly constituted compounds possessing the same configuration are in general influenced similarly by the same changes in the external conditions and also by the introduction of the same substituent into a given radicle attached to the asymmetric carbon atom."

Both methods have now been used by W. Leithe[19] for a determination of the configuration of coniine and α-pipecoline in terms of amino-acids which are standards of reference. Willstätter on the one hand showed that (+)*-conhydrine (VI) by oxidation gave a lævorotatory (—)-pipecolinic acid (VII); on the other hand, K. Löffler and G. Friedrich[20] showed that (+)-conhydrine could be converted through β-coniceine (VIII) into (—)-coniine (IX), so that (+)-coniine corresponded in configuration to (+)-pipecolinic acid. This acid, however, by an application of Clough's principles has been


(VII.) (VI.) (VIII.) (IX.)

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[17] *Ber.*, 1914, **47**, 2027; *A.*, 1914, i, 924.

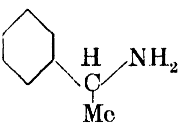
[18] *J.*, 1918, **113**, 526; *A.*, 1918, ii, 255. [19] *Ber.*, 1932, **65**, 927; *A.*, 865.

[20] *Ibid.*, 1909, **42**, 107; *A.*, 1909, i, 180.

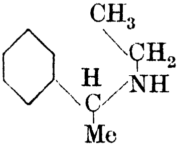
* (+) and (—) indicate the observed signs of rotation of the materials under discussion. Compare A. Wohl and K. Freudenberg, *Ber.*, 1923, **56**, 309; *A.*, 1923, i, 182.

shown to belong to the *d*-series of amino-acids. (+)-Pipecoline (2-methylpiperidine) is also spatially related to (+)-coniine, as is shown by the analogous optical behaviour of the bases in solvents and as salts, so that (+)-coniine, (+)-pipecoline, and (+)-pipecolinic acid belong stereochemically to the *d*-series of amino-acids.

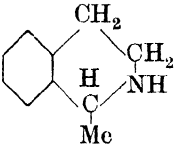
In a somewhat similar manner W. Leithe [21] has been able to determine the configuration of α-phenylethylamine and of bases of the type of laudanosine and tetrahydroberberine. When (—)-α-phenylethylamine (X) is benzoylated and the benzoyl product made susceptible to oxidation by introduction of a hydroxyl group in the phenyl nucleus, it can be oxidised to *l*(+)-benzoylalanine identical with that prepared from natural *l*(+)-alanine. (—)-α-Phenylethylamine has therefore the *l*-configuration. Now bases of the laudanosine and tetrahydroberberine type may be regarded as substituted α-phenylethylamines, as the following formulæ (X—XIII) show.



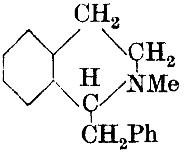
(X.)



(XI.)



(XII.)



(XIII.)

On this basis Leithe, using Clough's principles, has shown that *l*(—)-phenylethylamine (X), its *N*-ethyl derivative (XI), (—)-1-methyltetrahydro*iso*quinoline (XII), (—)-protolaudanosine (XIII), and (—)-tetrahydroprotoberberine are all configurationally similar and thus belong to the *l*-alanine series.

During the past year two attempts have been made to classify the complex stereochemical system of cinchona alkaloids with their four asymmetric centres.[22] Consideration of cases of resolution of such substances as 1-methyl*cyclo*hexylideneacetic acid of Pope, Perkin, and Wallach, where there is no asymmetric carbon atom, raises doubts as to the legitimacy of attributing particular signs of rotation to asymmetric centres in such substances as the cinchona alkaloids. The results obtained, however, when accepted with reserve do seem to justify the means adopted. P. Rabe [23] with a wealth of experimental material accumulated over a span of years has followed the methods used by H. King and A. D. Palmer [24] in deducing the sign of the contribution of the asymmetric centres in these alkaloids, arrives at the same conclusions, and has been able to classify sixteen closely related alkaloids. The principles involved are briefly these. The cinchona alkaloids of general formula (XIV) all give rise to weakly rotatory "toxines" (XV),

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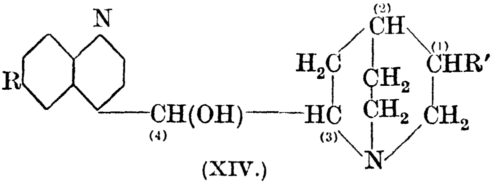
[21] *Ber.*, 1931, **64**, 2827; *A.*, 177.

[22] Compare J. Kenner, *Ann. Reports*, 1922, **19**, 157.

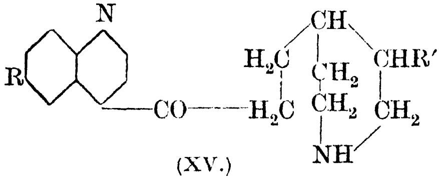
[23] *Annalen*, 1932, **492**, 242; *A.*, 289.

[24] *J.*, 1922, **121**, 2577.



(XIV.)

the same "toxine" being obtainable from four stereoisomeric alcohols (XIV). Thus hydrocinchonine, hydrocinchonidine, *epi*hydrocinchonine, and *epi*hydrocinchonidine, where $R = H$, $R' = Et$, all give rise to the same hydrocinchotoxine, so that the



(XV.)

differences between the alkaloids must lie in the spatial arrangement around carbon atoms 3 and 4. Hydrocinchonine and *epi*hydrocinchonine give rise by two different experimental methods to the same highly dextrorotatory deoxyhydrocinchonine, where $-CH(OH)-$ has been replaced by $-CH_2-$ just as hydrocinchonidine and *epi*hydrocinchonidine give rise to an isomeric deoxyhydrocinchonidine of lævorotation. The assumption is therefore made that the asymmetric carbon atom 3 is dextrorotatory in its contribution in the former pair of alcohols and lævorotatory in the latter pair. Hydrocinchonine and *epi*hydrocinchonine can thus only differ in the arrangement around carbon atom 4, and the same applies to hydrocinchonidine and *epi*hydrocinchonidine. Another assumption is now necessary. It is assumed that, since hydrocinchonine has a high dextrorotation and *epi*hydrocinchonine a low dextrorotation, carbon atom 4 is dextrorotatory in its contribution in hydrocinchonine and lævorotatory in its contribution in *epi*hydrocinchonine; similarly, since *epi*hydrocinchonidine has a dextrorotation and hydrocinchonidine a lævorotation, carbon atom 4 is dextrorotatory in the former and lævorotatory in the latter. The same reasoning has been applied by Rabe and his pupils to sixteen of these closely related bases, all of the general formula (XIV), with the following results.

	Optical sign of			Optical sign of	
	C3.	C4.		C3.	C4.
R = OMe; R′ = CH:CH$_2$.			R = OMe; R′ = Et.		
Quinine	—	—	Hydroquinine	—	—
*epi*Quinine	—	+	*epi*Hydroquinine	—	+
*epi*Quinidine..............	+	—	*epi*Hydroquinidine	+	—
Quinidine	+	+	Hydroquinidine	+	+
R = H; R′ = CH:CH$_2$.			R = H; R′ = Et.		
Cinchonidine	—	—	Hydrocinchonidine	—	—
*epi*Cinchonidine	—	+	*epi*Hydrocinchonidine	—	+
*epi*Cinchonine	+	—	*epi*Hydrocinchonine ...	+	—
Cinchonine	+	+	Hydrocinchonine	+	+

It will be noted that in the eight common naturally-occurring alkaloids the sign of rotation attributed to carbon atom 3 is always the same as that of carbon atom 4. In further justification of this system of classification it may be pointed out that the same result for the eight common alkaloids may be arrived at from a consideration of the magnitude of the specific rotations alone of the four isomeric bases in any one group; quinine and quinidine, for example, have the highest and the lowest lævo- and dextro-rotations respectively of the four isomerides.

P. Rabe and S. Riza [25] have extended the results to the four stereoisomeric rubanols (XIV; R = R′ = H), obtained by synthetic methods, in which carbon atom 1 has lost its asymmetry, and have again obtained concordant results.

A different view is adopted by H. Emde [26] but on a less satisfactory basis. He invokes the principle of optical superposition in a form used by Hudson and then abandons its legitimate deductions. Cinchona alkaloids only occur in nature in two out of the possible sixteen optically active forms and since, according to Emde, all examples of epimerism among naturally occurring substances are due to secondary carbinol groups, this must be the case in the cinchona alkaloids. The asymmetric centre 3 must therefore have the same configuration in all the naturally occurring alkaloids and the observed isomerism must be entirely dependent on the spatial arrangement around carbon atom 4. On such a basis it is difficult to see how Emde would approach the problem of the configuration of carbon atoms 3 and 4 in the epimeric bases.

Dipole measurements have been invoked [27] in determining the spatial arrangements around the sulphur atoms in thianthren

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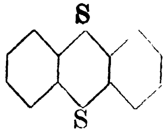
[25] *Annalen*, 1932, **496**, 151; *A.*, 865.

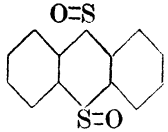
[26] *Helv. Chim. Acta*, 1932, **15**, 557; *A.*, 759.

[27] E. Bergmann and M. Tschudnowsky, *Ber.*, 1932, **65**, 458; *A.*, 507.

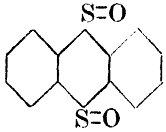
(XVI) and the two isomeric disulphoxides (XVII) and (XVIII) with dipole moments respectively of 1·68, 1·7, and 4·2.



(XVI.)



(XVII.)



(XVIII.)

Thianthren cannot be planar and it is supposed that the molecule is slightly folded at the sulphur atoms. The disulphoxide of structure (XVII) has practically the same dipole moment as thianthren, since the moments of the SO groups compensate one another. In (XVIII), however, the SO groups reinforce one another. It naturally follows that the oxygen atoms cannot be in the same plane as the CS bonds. A similar conclusion has of course already been reached through the resolution of sulphoxides by Phillips and Kenyon. The German workers are, however, loth to accept the postulate of semipolar double bonds as an explanation of the phenomena, as in their opinion the formation of a decet of electrons around the sulphur atom is not excluded.

Oxide Rings in Natural Products.

Fish Poisons.—This group of natural poisons has attracted considerable attention during recent years through the need for efficient insecticides. An arrow poison used by the Malays under the name Ipoh is said to be obtained from *Derris elliptica* (Fam. *Leguminosæ*), known to the Javanese as *tuba* root and employed by them as a fish poison. The active principle, tubatoxin, was first isolated by T. Ishikawa [28] and later shown by T. Kariyone, K. Atsumi, and M. Shimada [29] to be identical with rotenone, first isolated by K. Nagai [30] from *Millettia taiwaniana* Hayata, obtained from Formosa.

Through the efforts of the chemists of four different nations the constitution of rotenone is now agreed to be (I). On gentle oxidation it readily loses two hydrogen atoms with formation of dehydrorotenone [31] (II). The latter substance can be saponified by alcoholic potassium hydroxide with formation of derrisic acid (III), with addition of two molecules of water, from which dehydrorotenone (II) is re-formed by the action of acetic anhydride,[32] possibly through formation of an intermediate lactone.

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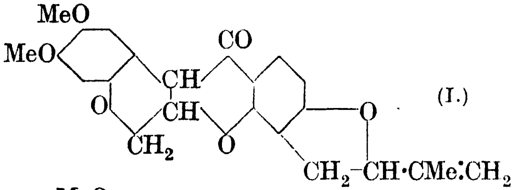
[28] *Jap. Med. Lit.*, 1917, **1**, 7; *A.*, 1918, i, 94.

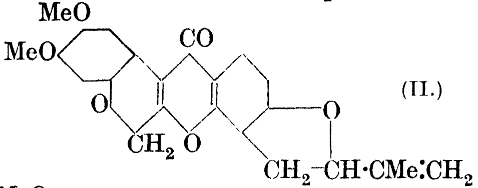
[29] *J. Pharm. Soc. Japan*, 1923, **500**, 739; *A.*, 1924, i, 250.

[30] *J. Tokyo Chem. Soc.*, 1902, **23**, 744.

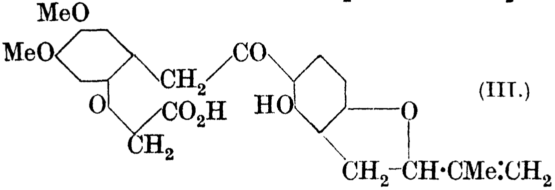
[31] A. Butenandt, *Annalen*, 1928, **464**, 253; *A.*, 1928, 1017.



(I.)

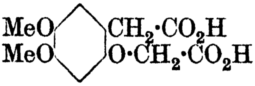


(II.)

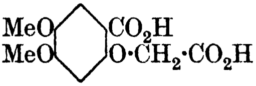


(III.)

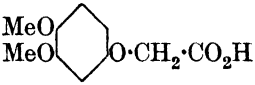
The molecule of derrisic acid is seen to be built up of two benzene nuclei with various addenda. When oxidised with hydrogen peroxide, derrisic acid yields derric acid [33] (IV), and on further oxidation with permanganate this gives the lower homologue, risic acid [34] (V), which can be decarboxylated to decarboxyrisic acid (VI).



(IV.)



(V.)



(VI.)

The constitutions deduced for these acids by LaForge have since been confirmed by syntheses of derric acid and risic acid by A. Robertson,[35] of risic acid by S. Takei, S. Miyajima, and M. Ono,[36] and of decarboxyrisic acid by LaForge.[37]

The determination of the constitution of the second half of the molecule of rotenone proved to be a more difficult problem. By the action of alcoholic potassium hydroxide on rotenone S. Takei [38] had obtained an acid called tubaic acid, now known to be $C_{12}H_{12}O_4$.[39] The constitution of tubaic acid (VII) was finally proved by H. L. Haller and F. B. LaForge [40] by a close study of its properties, although much supplementary experimental evidence was supplied by S. Takei and his co-workers.[41] Tubaic acid was optically active and contained a hydroxyl group, an indifferent oxygen atom, and a double bond which could readily be reduced, yielding dihydrotubaic acid. On further hydrogenation it gave tetrahydrotubaic acid (VIII), which could be decarboxylated to 2-*iso*amylresorcinol (IX).

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[32] F. B. LaForge and H. L. Haller, *J. Amer. Chem. Soc.*, 1932, **54**, 813; *A.*, 401.

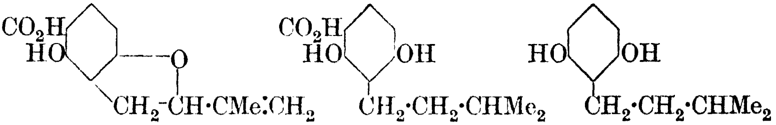
[33] F. B. LaForge, *ibid.*, 1931, **53**, 3896; *A.*, 1931, 1415.

[34] F. B. LaForge and L. E. Smith, *J. Amer. Chem. Soc.*, 1930, **52**, 2878 *A.*, 1930, 1187; S. Takei, S. Miyajima, and M. Ono, *Ber.*, 1931, **64**, 248; *A.*, 1931, 490.

[35] *J.*, 1932, 1380; *A.*, 751.

[36] *Ber.*, 1932, **65**, 1041; *A.*, 860.

[37] *J. Amer. Chem. Soc.*, 1931, **53**, 3896; *A.*, 1931, 1415.



(VII.) (VIII.) (IX.)

The orientation of groups in (IX) is established, since it is known that alkyl groups meta to hydroxyl groups inhibit the fluorescein test and one of the hydroxyl groups in (VIII) is indifferent to methylating agencies. The loss of optical activity observed when (VII) is converted into (VIII) shows that the *iso*propenyl side-chain is attached as shown and not to the neighbouring carbon atom.

The constitutions of the two halves of the rotenone molecule having been determined with a considerable degree of certainty, a satisfactory formula (I) was suggested almost simultaneously by F. B. LaForge and H. L. Haller,[42] by A. Robertson,[43] by S. Takei, S. Miyajima, and M. Ono,[44] and by A. Butenandt and W. McCartney.[45]

The numerous degradation products have almost all been assigned constitutions which in some cases have been confirmed by elegant partial syntheses. Thus, when rotenone is treated with zinc dust and alkali, it yields derritol [46] (X) with a loss of two carbon atoms. The properties of this substance are consistent with the structure shown, for when treated with ethyl chloroacetate it yields derrisic acid (III) mixed with dehydrorotenone[47] (II). The constitution of rotenonone, a product of strong oxidation of dehydrorotenone

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[38] *J. Chem. Soc. Japan*, 1923, **44**, 841; *Biochem. Z.*, 1925, **157**, 1; *A.*, 1925, i, 761.

[39] T. Kariyone and S. Kondo, *J. Pharm. Soc. Japan*, 1925, **518**, 376.

[40] *J. Amer. Chem. Soc.*, 1931, **53**, 4461; 1932, **54**, 1988; *A.*, 165, 739.

[41] *Ber.*, 1928, **61**, 1103; 1929, **62**, 3030; *A.*, 1928, 765; 1930, 216.

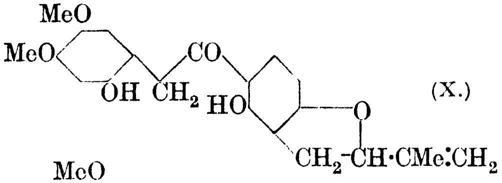
[42] *J. Amer. Chem. Soc.*, 1932, **54**, 810; *A.*, 401.

[43] *J.*, 1932, 1380; *A.*, 751.

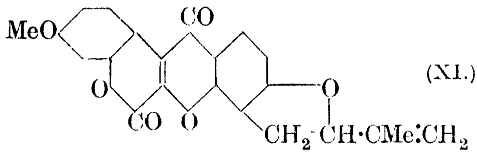
[44] *Ber.*, 1932, **65**, 1044; *A.*, 860.

[45] *Annalen*, 1932, **494**, 17; *A.*, 619.

[46] A. Butenandt, *ibid.*, 1928, **464**, 259; *A.*, 1928, 1017.



(X.)



(XI.)

and differing from it by the substitution of an oxygen atom for two hydrogen atoms, has been finally solved by the observation that rotenonone is hydrolysed almost quantitatively by alcoholic potassium hydroxide into derritol (X) and oxalic acid.[47] Conversely, rotenonone has been synthesised from derritol (X) and ethyl oxalate or chloro-oxalyl ethyl ester, so its constitution must be that represented by (XI).[47, 48]

In the practical application of derris extracts as insecticides it was observed by American workers that extracts poor in rotenone could be very active insecticides. E. P. Clark, following up the clue, showed that derris roots also contained toxicarol, deguelin, and tephrosin,[49] the first two of which at a dilution of 1 in 5×10^6 will kill goldfish in 3 or 4 hours. Clark was also able to show that *cubé*, a Peruvian fish poison, contained rotenone, tephrosin, and deguelin and that *Tephrosia toxicaria* from British Guiana contained toxicarol and deguelin,[50] whilst *T. vogelii* from Africa and Sumatra contained tephrosin and deguelin,[51] an observation made independently by A. Butenandt and G. Hilgetag.[52]

There is a close similarity in the molecular formulæ of these substances, suggesting a phytochemical relationship. Such is the case, for E. P. Clark has shown that all three substances give the same derric and risic acids as were obtained from rotenone.[53] The constitution of deguelin (XII) has been determined by Clark.[54]

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[47] S. Takei, S. Miyajima, and M. Ono, *Ber.*, 1932, **65**, 1043; *A.*, 860.

[48] F. B. LaForge, *J. Amer. Chem. Soc.*, 1932, **54**, 3377; *A.*, 1039.

[49] *Science*, 1930, **71**, 396; *A.*, 1930, 967.

[50] *J. Amer. Chem. Soc.*, 1930, **52**, 2461; *A.*, 1930, 1223.

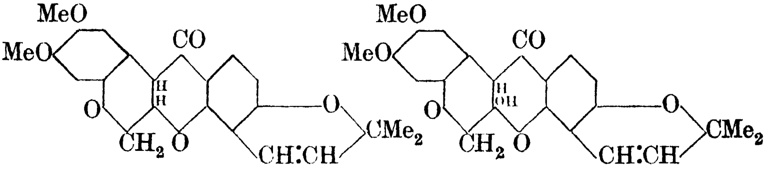
[51] *Ibid.*, 1931, **53**, 729; *A.*, 1931, 491.

[52] *Annalen*, 1932, **495**, 172; *A.*, 751.

[53] *J. Amer. Chem. Soc.*, 1932, **54**, 1600; *A.*, 619.

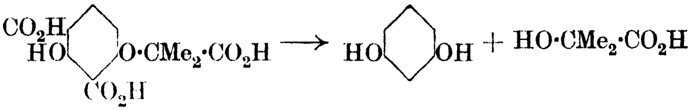
[54] *Ibid.*, p. 3002; *A.*, 950.

It passes on gentle oxidation with loss of two hydrogen atoms into dehydrodeguelin, which is also obtained by dehydration with acetic



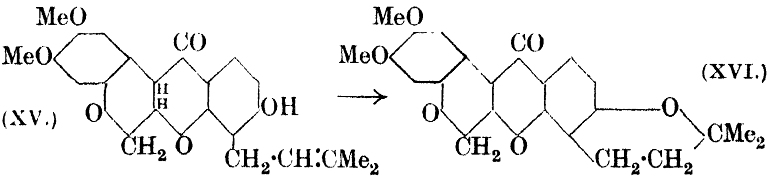
(XII.) (XIII.)

anhydride of tephrosin (XIII) and *iso*tephrosin.[55] In these two substances the relative positions of the added elements of the water molecule are undecided. Dehydrodeguelin, which is optically inactive, on oxidation with permanganate yields a new tricarboxylic acid, nicouic acid, $C_{12}H_{12}O_8$, which at its melting point loses α-hydroxy*iso*butyric acid. As it also gives the fluorescein reaction for resorcinol and yields the latter on boiling with aniline, the constitution (XIV) is assigned to it.



(XIV.)

Furthermore, when rotenone is reduced catalytically, it gives together with other products a so-called rotenonic acid [56] (XV), which was shown by H. L. Haller [57] to isomerise under the influence of acetic and sulphuric acids into β-dihydrorotenone (XVI) isomeric with dihydrorotenone. β-Dihydrorotenone on gentle oxidation gave dehydro-β-dihydrorotenone, which proved to be identical with dihydrodehydrodeguelin obtained by Clark by catalytic reduction of dehydrodeguelin.



(XV.) (XVI.)

These observations prove conclusively that the oxide ring in the second half of the molecule is a six-membered ring as shown. The same constitutions for deguelin and tephrosin on the basis of Clark's experimental results have also been advanced by A. Robertson [58] and by A. Butenandt and H. Hilgetag.[59] The constitution of toxicarol is still unsettled, the formulæ proposed by Clark [60] and by Butenandt and Hilgetag [59] showing considerable difference.

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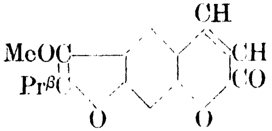
[55] E. P. Clark and H. V. Claborn, *J. Amer. Chem. Soc.*, 1932, **54**, 4455.

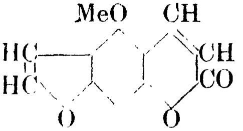
[56] F. B. LaForge and L. E. Smith, *ibid.*, 1929, **51**, 2574; *A.*, 1181.

[57] *Idem, ibid.*, 1931, **53**, 733; *A.*, **1931**, **491**.

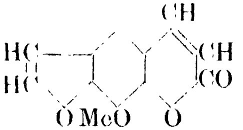
From the solution of the constitution of these fish poisons and insecticides arises the interesting and practical question as to the simplest structure which retains these properties. Peucedanin, a bitter principle from *Peucedanum officinale*, is known to be a fish poison [60a] and recently [60b] its constitution has been elucidated as (XVII). Still simpler structures but of the same type are possessed by bergapten (XVIII) and xanthotoxin (XIX), which are also known to be fish poisons.[61]

(XVII.)





(XVIII.)



(XIX.)

Cannabinol.—A resinous secretion of Indian hemp (*Cannabis Indica*) is known as hashish or bhang and has been used as an intoxicating drug for centuries in the East. By fractional distillation of the resin, T. B. Wood, W. T. N. Spivey, and T. H. Easterfield [62] were able to isolate a series of substances, one of which, a high-boiling oil, they concluded to be the active principle. Cannabinol is a constituent of this oil and is isolated as its crystalline acetyl derivative. On oxidation of the active fraction with nitric acid, nitrocannabinolactone, $C_{11}H_{11}O_4N$, was obtained, from which cannabinolactone, $C_{11}H_{12}O_2$, was isolated by removal of the nitro-group. Cannabinolactone gave *m*-toluic acid on fusion with potassium hydroxide. The constitution of cannabinolactone has now been definitely determined by R. S. Cahn [63] and confirmed by F. Bergel and K. Vögele [64] by synthesis. Cahn found that nitrocannabinolactone could be converted into the corresponding hydroxycannabinolactone, which on fusion with potassium hydroxide gave 6-hydroxy-*m*-toluic acid (I), identical with the synthetic material, and acetone. Wood, Spivey, and Easterfield were also able to oxidise cannabinolactone to cannabinolactonic acid (II), which Cahn has shown to be further oxidised to trimellitic acid, benzene-1 : 2 : 4-tricarboxylic acid, whence it follows that cannabinolactone must be represented by (III). The synthesis by F. Bergel and K. Vögele [64] starts from *p*-cymene-3-carboxylic acid (IV), which is oxidised by chromic acid to cannabinolactone (III) and other products. On further oxidation of the synthetic material with alkaline permanganate cannabinolactonic acid (II) was produced identical with a product obtained by G. Bargellini and G. Forli-Forti [65] from 4-aminodimethylphthalide [63] and also identical with an acid obtained from santonin by Cannizzaro and Gucci.

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[58] *J.*, 1932, 1384; *A.*, 751.

[59] *Annalen*, 1932, **495**, 172; *A.*, 751.

[60] *J. Amer. Chem. Soc.*, 1932, **54**, 2537; *A.*, 855.

[60a] Trier, "Chem. d. Pflanzenstoffe," 1924, 268.

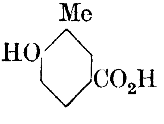
[60b] E. Späth, K. Klager, and C. Schlösser, *Ber.*, 1931, **64**, 2203; *A.*, 1931, 1298.

[61] C. Pomeranz, *Monatsh.*, 1893, **14**, 29; H. Thoms and E. Baetcke, *Ber.*, 1912, **45**, 3705; *A.*, 1913, i, 192.

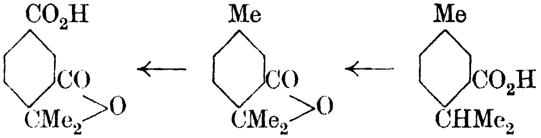
[62] *J.*, 1899, **75**, 20.

[63] *J.*, 1930, 986; 1931, 630; 1932, 1342; *A.*, 1930, 913; 1931, 625; 1932, 747.

[64] *Annalen*, 1932, **493**, 250; *A.*, 382.

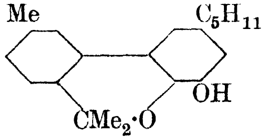


(I.)



(II.) (III.) (IV.)

The constitution of cannabinol has not been determined with certainty, but sufficient is known to make the constitution (V) possible.[63] Cannabinol can be acetylated, forms a methyl ether, and can be oxidised to *n*-hexoic acid, a product previously reported by earlier observers as being obtainable from crude high-boiling *cannabis* resins. The positions assigned to the hydroxyl and the *n*-amyl group are in accord with the products of oxidation and nitration and with the observation that cannabinol does not react with diazomethane in ethereal solution and does not dissolve in sodium hydroxide solution.



(V).

Simple Furan Derivatives.—Y. Asahina and collaborators [66] showed that *elsholtzione*, a ketone obtained from the essential oil of *Elsholtzia cristata*, Willdenow, was almost certainly 3-methyl-2-furyl *iso*butyl ketone (I).

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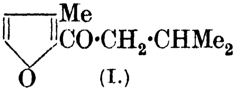
[65] *Gazzetta*, 1910, **40**, ii, 74; *A.*, 1910, i, 744.

[66] *Arch. Pharm.*, 1914, **252**, 435; *A.*, 1915, i, 429; *J. Pharm. Soc. Japan*, 1922, **485**, 565; *A.*, 1922, i, 1047; *Acta Phytochim.*, 1924, **2**, 1; *A.*, 1924, i, 976.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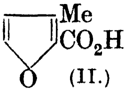
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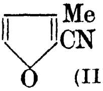
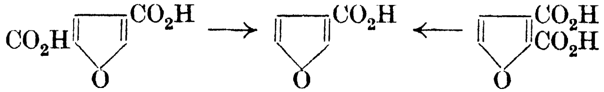
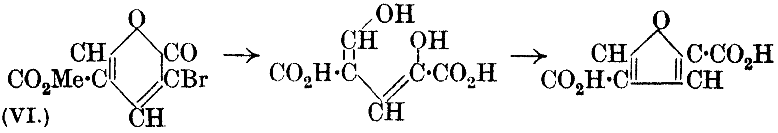

(III.)

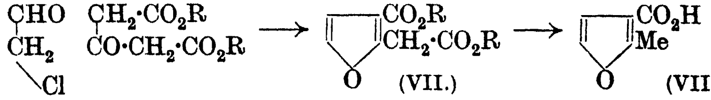
This has been confirmed by its synthesis [67] from β-methylfuran, which by Gattermann's method gave 3-methylfurfuraldehyde and this on oxidation gave elsholtzic acid (II) identical with an acid obtained from elsholtzione by Asahina. 3-Methylfurfuraldehyde was converted through its oxime into the nitrile (III), and a synthesis of elsholtzione (I) effected by allowing the nitrile to react with *iso*butylmagnesium bromide.[67]

T. Reichstein and H. Zschokke [68] have also synthesised furan-β-carboxylic acid in two ways and have shown that it is identical with the naturally occurring furan-β-carboxylic acid isolated by H. Rogerson from *Euonymus atropurpureus*.[69] The synthesis in each case depends on the partial decarboxylation of furandicarboxylic acids (IV) and (V) with loss of the carboxyl group in the α-position. The former dicarboxylic acid was obtained by F. Feist [70] by the action of potassium hydroxide on methyl bromocoumalate (VI). The second synthesis depends on the intermediate synthesis of the diethyl ester of 3-carboxyfuryl-2-acetic acid (VII) by condensation of chloroacetaldehyde and ethyl acetonedicarboxylate. This ester on saponification and decarboxylation gave 2-methylfuran-3-carboxylic acid (VIII), which could be oxidised to furan-2 : 3-dicarboxylic acid.

(IV.)


(V.)


(VI.)


(VII.)

(VIII.)

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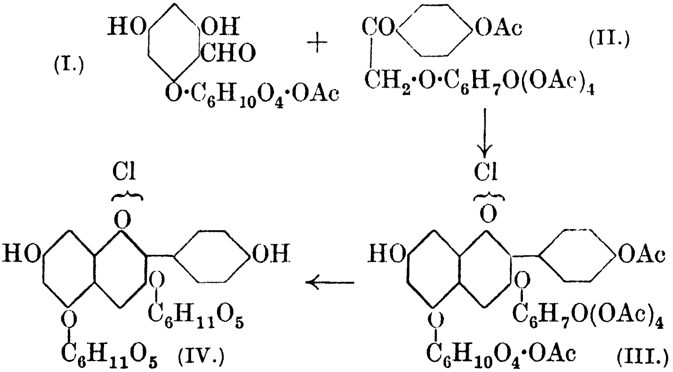
[67] T. Reichstein, H. Zschokke, and A. Goerg, *Helv. Chim. Acta*, 1931, **14**, 1277; *A.*, 166.

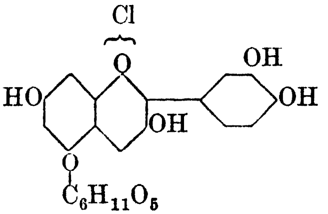
[68] *Ibid.*, 1932, **15**, 268; *A.*, 519.

[69] *J.*, 1912, **101**, 1044.

[70] *Ber.*, 1901, **34**, 1992; *A.*, 1901, 557.

Anthocyanins.—The past year has witnessed the culminating point in the chemistry of the anthocyanins. R. Robinson and A. R. Todd [71] have succeeded in synthesising the five diglucosides known as hirsutin, malvin, pelargonin, peonin, and cyanin chlorides, identical with the products from natural sources. All prove to be β-diglucosides substituted in the 3- and the 5-position of the anthocyanidin nucleus. Great experimental difficulties had to be overcome in the preparation of the intermediates, which when once obtained were condensed in the usual manner, of which the synthesis of pelargonin may be taken as a typical example. 2-*O*-Monoacetyl-β-glucosidylphloroglucinaldehyde (I) and ω-*O*-tetraacetyl-β-glucosidoxy-4-acetoxyacetophenone (II) were condensed in dry ethyl acetate by hydrogen chloride. The resulting flavylium salt (III) was kept in alkali in a hydrogen atmosphere to remove acetyl groups and acidified. Pelargonin chloride (IV) then separated in a state of purity.





(V.)

In a similar manner, by use of the appropriate initial materials cyanenin chloride (V) and malvenin chloride, the partial hydrolytic products of cyanin and malvin chlorides have been synthesised.[72]

If confirmation were needed of the view that malvin is a diglucoside containing the glucose residues attached to different hydroxyl groups, such has been furnished by P. Karrer and G. de Meuron.[73] Karrer and his collaborators had previously [74] shown that anthocyanins could be oxidised by hydrogen peroxide and that in two cases it was possible to isolate crystalline intermediate products, malvone and hirsutone, from malvin and hirsutin respectively. A re-investigation of malvone and hirsutone by Karrer and de Meuron has demonstrated that these ketones readily give a quantitative yield of syringic acid and glucose by solution in 2*N*-sodium hydroxide at room temperature. If treated with phenylhydrazine, they readily give up one molecule of glucose as phenylhydrazone and on acid hydrolysis of the residue the remaining glucose group may be found. For this reason malvone (VI; R = H) and hirsutone (VI; R = Me) are now regarded as esters of glucose and of syringic acid, with glucose attached to different parts of the molecule.

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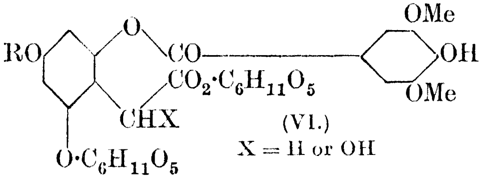
[71] *J.*, 1932, 2293, 2299, 2488; *A.*, 1140.

[72] A. León and R. Robinson, *J.*, 1932, 2221; *A.*, 1038.



(VI.)

X = H or OH

By application of the phenylhydrazine test to the solutions containing the hydrogen peroxide oxidation products of peonin, cyanin, and monardin it has been demonstrated that these three anthocyanins also contain two glucose groups in different positions in the molecule and one of them must be attached to position 3, a conclusion in agreement with the syntheses of Robinson and Todd.

Nitrogenous Anthocyanins.—In 1918 R. Willstätter and G. Schudel showed how many pigments, rosaniline, methylene-blue, and others, could be removed from aqueous solution by extraction with an organic solvent containing picric or dichloropicric acid.[75] This technique was applied by Schudel [76] to the colouring matter of beetroot (*Beta vulgaris*) and resulted in the isolation of an unstable nitrogenous diglucosidic anthocyanin, named betanin chloride, which gave betanidin chloride on hydrolysis. Similar pigments were found in *Celosia cristata* and in winter-spinach (*Atriplex hortensis atrosanguineus*).

On the synthetic side L. R. Ridgway and R. Robinson [77] had prepared 3-carbethoxyamino-4′-methoxy-8-ethoxy-2-phenylbenzopyrylium chloride (VII) from 2-hydroxy-3-ethoxybenzaldehyde and ω-carbethoxyamino-*p*-methoxyacetophenone, but attempts to obtain the 3-aminoflavylium salt were unsuccessful, the amino-group being replaced by hydroxyl. R. Robinson and (Mrs.) A. M. Robinson[78] have now succeeded in preparing pure 4′-aminoflavylium perchlorates (VIII) and (IX) by use of 4-aminoacetophenones.

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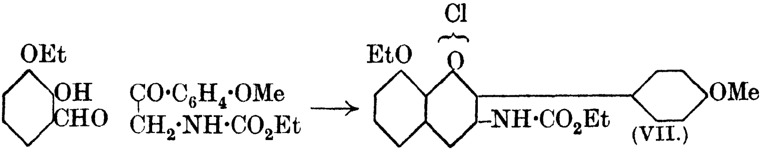
[73] *Helv. Chim. Acta*, 1932, **15**, 507, 1212; *A.*, 520.

[74] *Ibid.*, 1927, **10**, 729; *A.*, 1927, 1197.

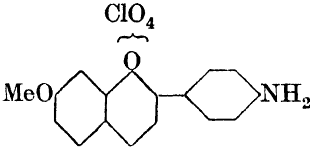
[75] *Ber.*, 1918, **51**, 782; *A.*, 1918, i, 399.

[76] *Dissert.*, Zürich.

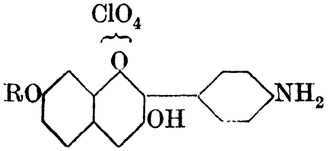
[77] *J.*, 1924, **125**, 2240; *A.*, 1925, i, 54.



(VII.)



(VIII.)



(IX.)

It is of interest that in these substances the amino-group is a better auxochrome than hydroxyl, and with this may be coupled the observation that betanidin is the bluest-red of all the anthocyanidins. The authors regard it as possible that the dihydroxyaminoflavylium salt (IX; R = H) may be identical with betanidin, since the colour reactions and the absorption spectra, in the visible region, of extracts of beet and atriplex in 0·1% hydrochloric acid and of 4′-amino-3 : 7-dihydroxyflavylium chloride showed close correspondence. Later unpublished work would, however, seem to suggest a possibility of betanidin being identical with a trihydroxyflavylium salt.[79]

Alkaloids.

Derivatives of Indole.—The developments in alkaloidal chemistry within the last few years have shown that there are a number of alkaloids containing the indole nucleus, derived presumably from tryptophan. The constitution of very few of these alkaloids is known with certainty; exceptions are physostigmine and the harmine group. The following account is confined to the more important developments in this field.

Ergot Alkaloids.—It may be recalled that for a number of years ergotoxine and ergotinine were the only two definitely recognised alkaloids of ergot. In 1922 A. Stoll[80] isolated a second pair of isomeric alkaloids, ergotamine and ergotaminine, which chemically and pharmacologically show very close similarities to the former pair of alkaloids. S. Smith and G. M. Timmis[81] were able to confirm the isolation of ergotamine and ergotaminine but only from unofficial ergots, such as that growing on a New Zealand *Festuca*. In 1931 the same observers showed that ergotoxine was accompanied by two alkaloids, ergotinine and ψ-ergotinine, the proportion varying in different ergots. Both ergotinine and ψ-ergotinine are converted into ergotoxine by boiling with alcohol and phosphoric acid and ψ-ergotinine is partly converted into ergotinine by boiling with methyl alcohol. The composition of these alkaloids is still doubtful. A. Soltys [82] gives good reasons for concluding that ergotamine and ergotaminine may be represented by the formula $C_{33}H_{35}O_5N_5$ and ergotinine by $C_{35}H_{39}O_5N_5$. He also finds all four alkaloids to be phenolic or weakly carboxylic, to yield ammonia on hydrolysis, and to give benzoic acid on oxidation with permanganate and *p*-nitrobenzoic acid on oxidation with nitric acid. W. A. Jacobs [83] confirms the latter observation on ergotinine and has isolated a new base, $C_{14}H_9O_8N$, containing three carboxyl groups and one *N*-methyl group by the action of nitric acid. On the other hand, Smith and Timmis [84] have shown that all four alkaloids on hydrolysis with alcoholic potassium hydroxide give ammonia and a base ergine, $C_{17}H_{21}ON_3$, which likewise contains one *N*-methyl group and gives many colour reactions associated with indole derivatives. The only other important observation bearing on the constitution of these alkaloids is the well-known one of G. Barger and A. J. Ewins,[85] that ergotoxine and ergotinine give *iso*butyrylformamide, $CHMe_2{\cdot}CO{\cdot}CO{\cdot}NH_2$, on heating. This is probably the amide group present in the molecule of these alkaloids which appears as ammonia on hydrolysis.

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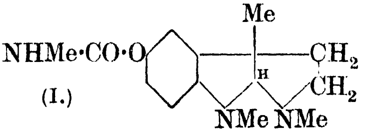
[78] *J.*, 1932, 1439; *A.*, 750.

[79] *Naturwiss.*, 1932, **33**, 613.

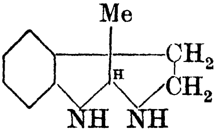
[80] *Schweiz. Apoth.-Ztg.*, 1922, **60**, 341; *A.*, 1923, i, 127.

[81] *J.*, 1930, 1393; 1931, 1888; *A.*, 1930, 1050; 1931, 1171.

Physostigmine.—The pioneering experimental work of G. Barger and E. Stedman [86] and of M. and M. Polonowski [87] led to the elucidation of the structure (I) now accepted for physostigmine (eserine). The greatest difficulty in the synthesis of such a structure might be anticipated in the closure of β-substituted dihydroindoles



(I.)



(II.)

with formation of the third ring. This has, however, been accomplished by three different methods which have led to the synthesis of structures related to or identical with those of physostigmine derivatives.

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[82] *Ber.*, 1932, **65**, 553; *A.*, 629.

[83] *J. Biol. Chem.*, 1932, **97**, 739; *A.*, 1147.

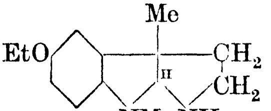
[84] *J.*, 1932, 763, 1543; *A.*, 526, 759.

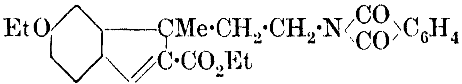
[85] *J.*, 1910, **97**, 290.

[86] *J.*, 1925, **127**, 247; *A.*, 1925, i, 392.

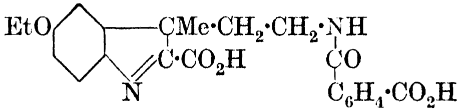
[87] *Compt. rend.*, 1924, **178**, 2078; **179**, 334; *A.*, 1924, i, 1094.

T. Hoshino and K. Tamura [88] allowed β-indolylethylamine to react with excess of methylmagnesium iodide (4 mols.) and treated the product with methyl iodide. A 30% yield of dinordeoxy-eseroline (II) was thus obtained. R. Robinson and H. Suginome,[89] after preliminary syntheses of indolenine derivatives, have been able to prepare *dl*-noreserethole (III) in an instructive manner.


(III.)


(IV.)

Ethyl δ-phthalimido-α-acetyl-β-methylvalerate was coupled with *p*-ethoxydiazonium chloride in alkaline solution to yield ethyl δ-phthalimido-α-keto-β-methylvalerate-*p*-ethoxyphenylhydrazone, $C_6H_4{:}(CO)_2{:}N{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}C(CO_2Et){:}N_2H{\cdot}C_6H_4{\cdot}OEt$, with loss of an acetyl group. When this hydrazone was submitted to the action of ethyl-alcoholic hydrogen chloride it gave ethyl 5-ethoxy-3-methyl-3-β-phthalimidoethylindolenine-2-carboxylate (IV). Saponification of this by ethyl-alcoholic potassium hydroxide gave a dicarboxylic acid (V) which on decarboxylation in boiling xylene gave the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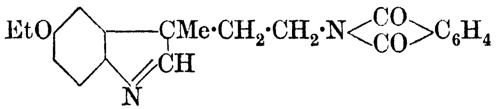
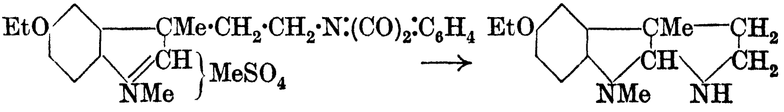

(VI.)

indolenine (VI). The methosulphate (VII) of (VI) was deprived of the phthalic acid by short boiling with hydrazine hydrate in alcoholic solution and on acidification cyclisation took place by simple addition of the amino-group in the side chain to the unsaturated indoleninium system with production of *dl*-noreserethole (VIII).

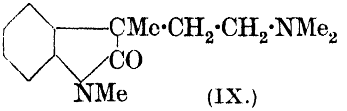

(VII.) (VIII.)

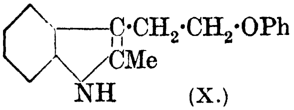
As two asymmetric centres are produced, a mixture of two racemates might be expected; but only one has been observed.

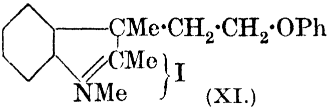
[88] *Proc. Imp. Acad. Tokyo*, 1932, **8**, 171; *A.*, 952.

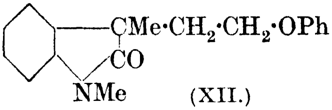
[89] *J.*, 1932, 304; *A.*, 287.

Yet another method for closing the third ring has been worked out by F. E. King and R. Robinson.[90] In a preliminary research H. S. Boyd-Barrett and R. Robinson [91] were able to prepare desethoxydehydroeseretholemethine (IX) by synthesising the indole (X) from γ-phenoxypropyl methyl ketone phenylhydrazone. This indole was methylated under pressure with methyl iodide to yield 1 : 2 : 3-trimethyl-3-β-phenoxyethylindoleninium iodide (XI), the base corresponding to which on oxidation with permanganate gave an indolinone (XII).

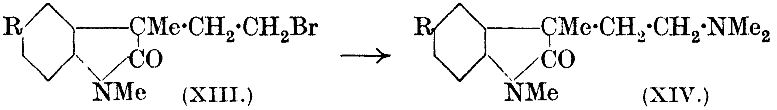

(IX.)


(X.)

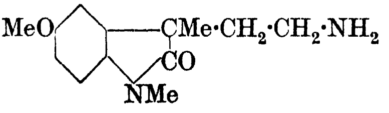

(XI.)

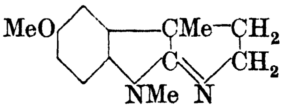

(XII.)

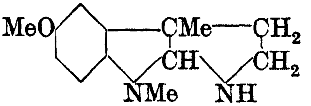
By the action of fuming hydrobromic acid this indolinone was converted into a reactive bromoethyl derivative (XIII; R = H), the bromine of which could be replaced by methylamino- or dimethylamino-groups with production in the latter case of desethoxydehydroeseretholemethine (XIV; R = H).


(XIII.) (XIV.)

By extending the synthesis to the corresponding methoxy-derivative (XIV; R = OMe), King and Robinson were able to synthesise and eventually resolve dehydroesermetholemethine, (XIV; R = OMe) into its optical isomerides, as the quaternary salt. One of these proved to be identical with the natural product, and incidentally the interpretation given to the various stages in the syntheses received confirmation. Cyclisation of ethylaminoindolinones was finally effected in a simple manner. The methoxybromide (XIII; R=OMe) was converted through its reaction product with phthalimide into the corresponding ethylamine (XV),


(XV.)


(XVI.)


(XVII.)

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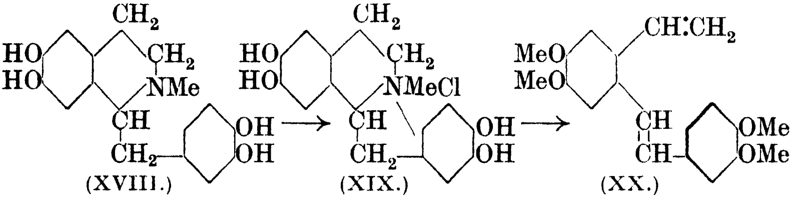
[90] *J.*, 1932, 1433; *A.*, 759.

[91] *Ibid.*, p. 317; *A.*, 287.

which was dehydrated by phosphoric acid in boiling xylene to form an amidine (XVI), and this on catalytic reduction gave noresermethole (XVII). The latter was characterised as a crystalline quaternary salt, *dl*-esermethole methopicrate, which showed a great similarity to the natural salt.

There is little doubt that physostigmine is derived in the plant from hydroxytryptophan. The possibility, however, of indole nuclei arising by oxidation of amino-acids is shown by the work of H. S. Raper [92] on the conversion of tyrosine and of 3 : 4-dihydroxyphenylethylmethylamine into indole derivatives under the influence of tyrosinase. A striking example of the somewhat analogous oxidation of a tertiary base into a quaternary salt by indole ring formation has been discovered by R. Robinson and S. Sugasawa.[93] Laudanosoline (XVIII) is oxidised by chloranil in alcoholic solution and in the presence of potassium acetate to a dehydrolaudanosoline hydrochloride, a quaternary dihydroindole (XIX) which contains the same carbon skeleton as laudanosoline, for on exhaustive methylation and Emde degradation it gives the same product (XX) as laudanosine itself. Almost the same ground was covered by C. Schöpf and K. Thierfelder,[94] who were able to effect the same dehydrogenation by tetrabromo-*o*-quinone, by oxygen in presence of platinum, and by potassium ferricyanide in presence of a phosphate buffer at p_H 6·9—7·1.



Strychnos Alkaloids.—During the past year great advances have been made in the elucidation of the structural formulæ of brucine and strychnine. The advances are such that, although further work is necessary to confirm the internal structure of the molecule, the main features of the outside skeleton may be regarded as settled. The two formulæ for brucine (R = OMe) and strychnine (R = H) which find most favour are the following :

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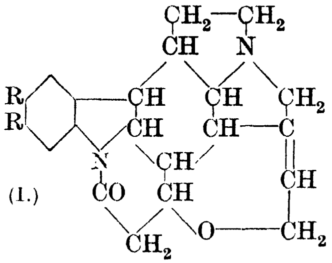
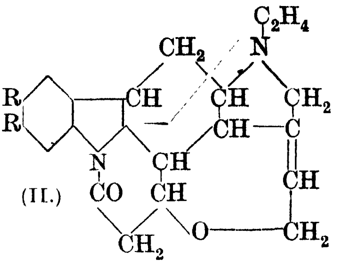
[92] *Biochem. J.*, 1927, **21,** 89; *A.*, 1927, 278. W. L. Dulière and H. S. Raper, *ibid.*, 1930, **24,** 239; *A.*, 1930, 814. Compare also H. Burton, *J.*, 1932, 546; *A.*, 402.

[93] *J.*, 1932, 789; *A.*, 527.

[94] *Annalen*, 1932, **497,** 22; *A.*, 1046.



(I.)



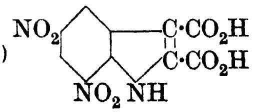
(II.)

(I) is that put forward by H. Leuchs[95] and it contains most of the features characteristic of the formula advanced by K. N. Menon and R. Robinson[96] except that the bridge from the basic N-atom in the Menon–Robinson formula is attached to the β-carbon atom of the dihydroindole structure. B. K. Blount and R. Robinson[97] prefer the structure (II) in which the bridge C_2H_4 may be interpreted as ·CHMe, in which case strychnine would contain the skeleton of tryptophan and also that of harmine. The arguments in favour of the positions assigned to the bridge are not conclusive and its final position must await further experimental work.

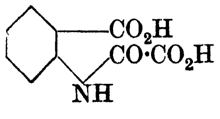
The measure of agreement expressed by these two formulæ is mainly a result of the interpretation of the experimental observations on the oxidation of these alkaloids with nitric acid, chromic acid, and permanganate.

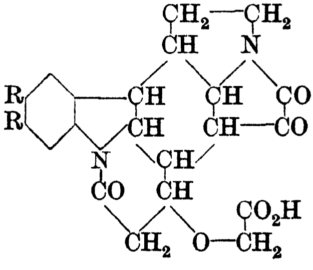
The important product of the oxidation of strychnine with nitric acid, named dinitrostrycholcarboxylic acid by Tafel, has been shown[96] to be 5 : 7-dinitroindole-2 : 3-dicarboxylic acid (III). This finds expression in the suggested formulæ and is in agreement with the results of E. Späth and H. Bretschneider,[98] who obtained *N*-oxalylanthranilic acid (IV) as a product of the oxidation of strychnine with permanganate in alkaline solution, and *N*-oxalyl-4 : 5-dimethoxyanthranilic acid from brucine. The permanganate oxidation of brucine in acetone solution was the subject of Leuchs'

(III.)



(IV.)





(V.)

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[95] *Ber.*, 1932, **65**, 1230; *A.*, 953.

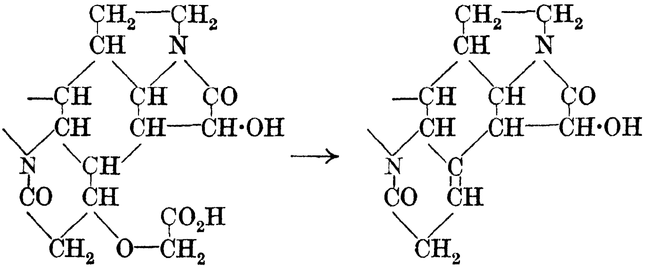
[96] *J.*, 1932, 780; *A.*, 527.

[97] *Ibid.*, p. 2305; *A.*, 1147.

[98] *Ber.*, 1930, **63**, 2997; *A.*, 1931, 242.

earliest contribution to the chemistry of these alkaloids, but the interpretation of the results was first correctly advanced by R. C. Fawcett, (the late) W. H. Perkin (jun.), and R. Robinson[99] and has now been accepted by H. Leuchs and F. Kröhnke.[1] Leuchs found that when brucine, $C_{23}H_{26}O_4N_2$, was oxidised by permanganate, a keto-acid, brucinonic acid (V), was formed which could be reduced by sodium amalgam to brucinolic acid (VI), and this by the action of alkali gave brucinolone (VII) and glycollic acid. Using formula (I) for simplicity of representation, the changes are as follows :

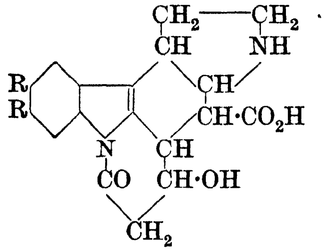
(V.) ↓ (VI.)

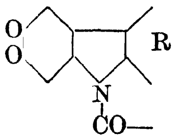


(VII.)

The characteristic feature of brucinonic acid (V) is its α-ketonic acid amide group and as such it should be oxidisable by hydrogen peroxide. H. Leuchs and F. Kröhnke[2] now find that such is the case, for an amino-acid, $C_{20}H_{22}O_6N_2$, possibly (VIII), is formed.

(VIII.)





(IX.)

A further striking degradation has now been recorded.[3] When brucinonic acid (V) or brucinolic acid (VI) is oxidised with chromic acid in sulphuric acid solution, a red crystalline *o*-quinone (IX) is formed, but the resinous by-products on further oxidation with the same reagent give a very small yield of an amino-acid, $C_{13}H_{16}O_5N_2$. The suggestion is made that this is formed by the destruction of the truly aromatic portion of the molecule, as happens in the preparation of Hanssen's acid, $C_{16}H_{20}O_4N_2$, from brucine, $C_{23}H_{26}O_4N_2$, together with loss of glycollic acid and oxidation of the α-ketonic acid amide group of brucinonic acid as already described. On this basis the natural result of the degradation is as shown below.

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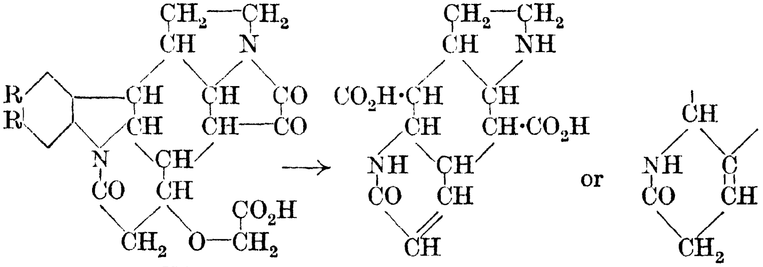
[99] *J.*, 1928, 3087; *A.*, 1929, 82.

[1] *Ber.*, 1932, **65**, 218; *A.*, 407.

[2] *Ibid.*, p. 980; *A.*, 866.

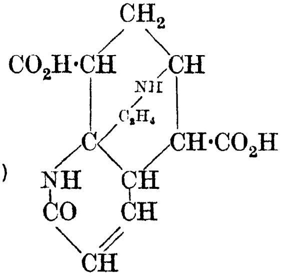
[3] *Ibid.*, p. 1230; *A.*, 953.

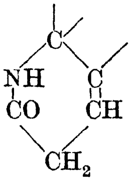


(V.) (X.) (X*a*.)

As is pointed out by Leuchs, a substance of formula (X) on oxidation with permanganate should yield 5-oxalylaminohexahydroindoline-4 : 6 : 7-tricarboxylic acid, which would give oxalic acid on hydrolysis. (X*a*) on the other hand should give a β-ketonic acid, namely, 5-malonylamino-6-ketohexahydroindoline-4 : 7-dicarboxylic acid, which should lose carbon dioxide and malonic acid on hydrolysis. On the basis of the Blount–Robinson formulæ, (X) and (X*a*) should be replaced by (XI) and (XI*a*).

(XI.)





(XI*a*.)

When strychnine is reduced electrolytically to tetrahydrostrychnine, the amide group $>N\cdot CO^-$ becomes $>NH,CH_2\cdot OH^-$ and it was shown[4] that on oxidation of this with chromic acid an amino-acid, $C_{21}H_{22}O_4N_2$, was formed in 14% yield. When hexahydrostrychnine was similarly oxidised,[5] an amino-acid, $C_{21}H_{22}O_4N_2$, resulted which was also obtained by catalytic reduction of Leuchs' acid. On this view Leuchs' acid should be $C_{21}H_{20}O_4N_2$. The changes involved, however, appeared to be complex, since the acid $C_{21}H_{22}O_4N_2$ of Briggs and Robinson formed a benzylidene derivative, and therefore presumably contained the reconstituted $>N\cdot CO\cdot CH_2^-$ group of strychnine, but did not give the usual strychnine colour reactions. It has now been demonstrated [6] that these acids, almost certainly, contain an extra carbon atom, present as a carboxyl group in the *p*-position to the indole N-atom and that it is derived from a double molecule analogous to the red amorphous dyes obtained by H. Wieland and collaborators [7] from strychnine and characterised as meriquinonoid diphenyl derivatives. This gives a satisfactory explanation of the origin of the new carboxyl group and of the failure to give the normal colour reactions, since these are dependent on a free *p*-position.

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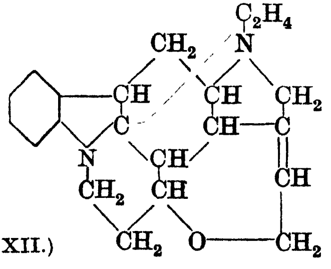
[4] H. Leuchs and W. Wegener, *Ber.*, 1930, **63**, 2220; *A.*, 1930, 1455; H. Leuchs, *ibid.*, p. 3187; *A.*, 1931, 242.

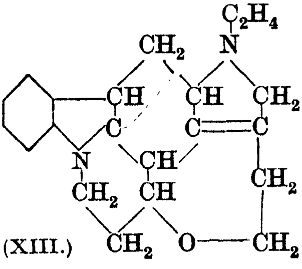
[5] L. H. Briggs and R. Robinson, *J.*, 1931, 3160; *A.*, 178.

The new formulæ for brucine and strychnine also give a satisfactory explanation of the *neo*-bases. When strychnidine methosalts (amide group reduced to $-NH{\cdot}CH_2-$) are digested with methyl-alcoholic potassium hydroxide, they yield a methoxymethyl-dihydrostrychnidine which can be interpreted by the scheme

$$>C{\cdot}NMe\}SO_4Me \longrightarrow >C{\cdot}OMe,\ NMe.$$

When the quaternary salt is reconstituted by boiling dilute acid, an isomeric methyl*neo*strychnidinium salt is formed which on heating loses methyl chloride, for instance, and gives *neo*strychnidine. Both strychnidine and *neo*strychnidine give the same dihydrostrychnidine on catalytic reduction, so the difference in the bases must reside in the position of the double bond.[8] Strychnidine (XII) and *neo*strychnidine (XIII) are therefore assigned the structures shown, the double bond occupying adjacent positions. The oxidation of *neo*strychnidine to the diketone strychnidone by permanganate,[9] on this view of the constitution, would consist in the disruption of the double bond by addition of two oxygen atoms with formation of a 10-membered ring.


(XII.)


(XIII.)

Subsidiary Strychnos Alkaloids.—The study of the constitution of the subsidiary alkaloids which accompany the chief alkaloid in a plant is of considerable importance, for it throws light on the general scheme of phytochemical synthesis adopted by nature in a given species. Within the last few years four new alkaloids have been isolated from the residues accumulated by manufacturers in the isolation of strychnine and brucine. Whether these new alkaloids are specific to *Strychnos Nux-vomica* or *Str. Ignatii* or both is unrecorded.

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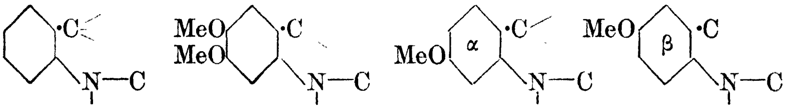
[6] H. Leuchs and H. Beyer, *Ber.*, 1932, **65**, 201; *A.*, 407.

[7] *Annalen*, 1931, **491**, 107; *A.*, 179.

[8] O. Achmatowicz, (the late) W. H. Perkin (jun.), and R. Robinson, *J.*, 1932, 486; *A.*, 406.

[9] G. R. Clemo, (the late) W. H. Perkin (jun.), and R. Robinson, *J.*, 1927, 1589; *A.*, 1927, 888.

In 1931 K. Warnat [10] described the isolation of three new strychnos alkaloids which he named α- and β-colubrines and ψ-strychnine. The first two differ in composition from strychnine by a methoxy-group and on oxidation by Späth and Bretschneider's method give two isomeric monomethoxyoxalylanthranilic acids. These were characterised as their dimethyl esters, that from α-colubrine being identical with synthetic dimethyl *N*-oxalyl-4-methoxyanthranilate and that from β-colubrine being identical with the isomeric 5-methoxy-derivative. This suggests that strychnine, brucine, and the two colubrines stand in the following relationship :



There is no proof of the identity of the remainder of the molecules with that contained in strychnine or brucine, but the similarity of properties of all four bases suggests identity.

The third alkaloid, ψ-strychnine, has been examined by B. K. Blount and R. Robinson [11] and the original preliminary observations of Warnat confirmed. Its composition is that of a hydroxystrychnine and on reduction in acid solution it yields strychnine. It is relatively stable to ferricyanide, forms an *N*-nitroso-derivative, and on crystallisation from methyl or ethyl alcohol yields methyl or ethyl derivatives which are readily hydrolysed in cold acid solution with formation of ψ-strychnine. These properties and others suggest that ψ-strychnine carries a tertiary alcohol group on a carbon atom adjacent to the basic N-atom in strychnine. On this view the nitrosoamine would be $>CO,NO{\cdot}N<$ and the ethers $>C(OR){-}N<$.

The fourth subsidiary alkaloid isolated from manufacturers' residual liquors is vomicine,[12] $C_{22}H_{24}O_4N_2$, differing from strychnine ($C_{21}H_{22}O_2N_2$) by CH_2O_2. It contains an aromatic ring, since it is easily brominated, and has one nitrogen in combination as a lactam, since boiling alcoholic potassium hydroxide gives vomicinic acid, $C_{22}H_{26}O_5N_2$, a substance which is very readily autoxidisable and is converted into the original base by the action of acids. On catalytic reduction vomicine adds on two hydrogen atoms, indicating the presence of a double bond. It readily forms a benzoyl derivative and on reduction with hydriodic acid gives deoxyvomicine, $C_{22}H_{24}O_3N_2$, these properties suggesting the presence of a tertiary alcoholic group. Unlike strychnine, vomicine does not add on methyl iodide at the basic N-atom, but vomicinic acid on methylation yields *N*-methylvomicinic acid and its methyl ester, together with two parallel products each containing a CH_2 group more, *viz.*, an acid $C_{24}H_{30}O_5N_2$ and an ester $C_{25}H_{32}O_5N_2$.[13] The acid $C_{24}H_{30}O_5N_2$ can be converted by alcoholic potassium hydroxide with difficulty into *N*-methylvomicinic acid. This suggests the presence of a phenolic group, which would also account for the ready autoxidation of vomicinic acid. This finds expression in the partial formula (I) for vomicine and (II) for vomicinic acid.

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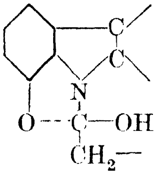
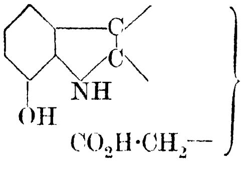
[10] *Helv. Chim. Acta*, 1931, **14**, 997; *A.*, 1931, 1312.

[11] *J.*, 1932, 2305; *A.*, 1147.

[12] H. Wieland and G. Oertel, *Annalen*, 1929, **469**, 193; *A.*, 1929, 708.

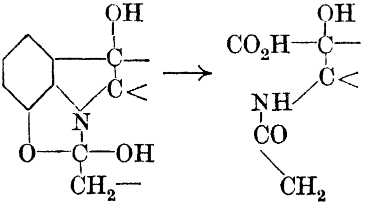
(I.)





(II.)

Vomicine, like brucine, is sensitive to chromic acid and gives an important series of degradation products.[14] The chief acid formed has the composition $C_{17}H_{22}O_5N_2$ and very readily loses carbon dioxide. The carboxyl group is therefore probably adjacent to a hydroxyl group. By analogy with the results obtained by the action of chromic acid on brucine and strychnine the degradation of vomicine may be represented thus :



The base $C_{16}H_{22}O_3N_2$ obtained on decarboxylation of this acid contains a hydroxyl group which can be benzoylated. It can also be reduced catalytically to $C_{16}H_{26}O_2N_2$, probably through reduction of a double bond and of the ether linkage :

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[13] H. Wieland and F. Calvet, *Annalen*, 1931, **491**, 117; *A.*, 179.

[14] H. Wieland and G. Oertel, *ibid.*, 1929, **469**, 193; *A.*, 1929, 708; H. Wieland, F. Hölscher, and F. Cortese, *ibid.*, 1931, **491**, 133; *A.*, 179.

$$>C{-}O{-}C< \longrightarrow -CH\quad CH\!< + H_2O.$$

The two extra oxygen atoms in vomicine which are not found in strychnine are thus accounted for as a tertiary alcohol group and a potential phenolic group. If the remainder of the ring systems of strychnine and vomicine is the same, and there is no evidence so far inconsistent with this view, the only additional difference will be in the possession by vomicine of an extra methyl group.

Yohimbine.—A group of alkaloids of which yohimbine is the chief representative has been obtained from *Corynanthe Johimbe*, of the natural order *Rubiaceæ* to which the cinchona plants belong. Six alkaloids, yohimbine, yohimbene,[15] *allo*yohimbine,[16] *iso*-yohimbine,[16] α-[17] and γ[18]-yohimbines, have been definitely identified and they all appear to have the formula $C_{21}H_{26}O_3N_2$. In addition, a seventh isomeric alkaloid, corynanthine, has been obtained by E. Fourneau and Fiore [19] from *Pseudocinchona africana*, of the same natural order as the above. All these alkaloids are monomethyl esters which on hydrolysis yield monocarboxylic acids, and four of them, yohimbine, yohimbene, γ-yohimbine, and *iso*-yohimbine, give isomeric acids which on decarboxylation yield one and the same alcohol, yohimbol.[20] *allo*Yohimbine gives an isomeric alcohol, *allo*yohimbol. Corynanthine and α-yohimbine give neither yohimbol nor *allo*yohimbol. The four alkaloids which give yohimbol, when treated with selenium and soda-lime in a vacuum sublimation apparatus, give one and the same substance, to which the formula $C_{19}H_{12}N_2{\cdot}O{\cdot}C_{19}H_{12}N_2$ is assigned by G. Hahn and W. Schuch,[20] but which according to F. Mendlik and J. P. Wibaut [21] is a base, $C_{19}H_{18}N_2$, to which the name yobyrine is given. The difference between the four alkaloids named must accordingly be due to a different situation for the carbomethoxy-group in the molecule.

A number of degradation products have been obtained from yohimbine, some of which have been identified. G. Barger and

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[15] G. Hahn and W. Brandenberg, *Ber.*, 1926, **59**, 2189; 1927, **60**, 707; *A.*, 1926, 1263; 1927, 471.

[16] *Idem, Ber.*, 1927, **60**, 669; *A.*, 1927, 471; K. Warnat, *ibid.*, 1926, **59**, 2388; 1927, **60**, 1118; *A.*, 1926, 1263; 1927, 681.

[17] R. Lillig and H. Kreitmair, *Merck's Jahresber.*, 1928, **42**, 20; *B.*, 1930, 485; G. Hahn, and W. Schuch, *Ber.*, 1930, **63**, 1638; *A.*, 1930, 1194.

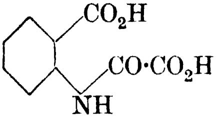
[18] G. Hahn and W. Schuch, *loc. cit.*

[19] *Bull. Soc. chim.*, 1911, [iv], **9**, 1037; *A*, 1912, i, 49.

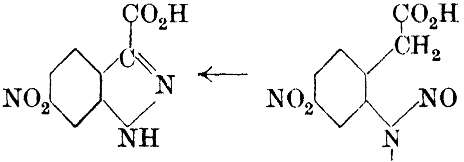
[20] *Ber.*, 1930, **63**, 1638, 2961; *A.*, 1930, 1194; 1931, 243.

[21] *Rec. trav. chim.*, 1931, **50**, 91; *A.*, 1931, 369.

(Miss) E. Field[22] showed that yohimboaic acid when distilled with lime gives a dimethylindole with an odour of scatole, and which gives a crystalline picrate. The same dimethylindole, m. p. 55°, was obtained by E. Winterstein and M. Walter[23] by distillation of the acid and by K. Warnat[24] by heating the acid with soda-lime or zinc dust. This indole is not identical with any known dimethylindole, and synthetic experiments by F. Mendlik and J. P. Wibaut[25] show that it is not identical with 3 : 5-, 3 : 6-, or 3 : 7-dimethylindole. The colour reaction of yohimbine with sulphuric acid and potassium dichromate is similar to that given by strychnine and suggests a relationship. In fact E. Späth and H. Bretschneider[26] find that both alkaloids on oxidation with alkaline permanganate give *N*-oxalylanthranilic acid (I). In the case of strychnine this acid is known to arise from an indole nucleus, but in the case of yohimbine a quinoline structure is not excluded.



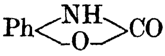
(I.)



(II.) (III.)

When yohimbine is boiled with acetic anhydride and sodium acetate, it gives a crystalline *ON*-diacetylyohimbine and an amorphous monoacetyl derivative.[27] The former on oxidation with dilute nitric acid gives succinic acid and a 6-nitroindazole-3-carboxylic acid (II), the constitution of which follows from its decarboxylation to 6-nitroindazole identical with the synthetic product.[28] The indazole structure is probably not present in the original molecule, but arises by the action of nitrous acid on an *o*-aminophenylacetic acid group as is shown in (III). The formation of the indazole is exactly analogous to the formation of 4-nitro-5-(3-pyridyl)-pyrazole from nicotine by the action of nitric acid.[29]

Two other degradation products of yohimbine which have been definitely identified are *o*-oxycarbanil,



$\mathrm{Ph}<^{\mathrm{NH}}_{\mathrm{O}}>\mathrm{CO}$, which is obtained by the action of permanganate on yohimboaic acid in dilute alkali at room temperature,[30] and *iso*quinoline, obtained in small yield by distillation of yohimboaic acid with zinc dust.[23]

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[22] *J.*, 1915, **107**, 1025.

[23] *Helv. Chim. Acta*, 1927, **10**, 577; *A.*, 1927, 1208.

[24] *Ber.*, 1927, **60**, 1118; *A.*, 1927, 681.

[25] *Rec. trav. chim.*, 1931, **50**, 91; *A.*, 1931, 369.

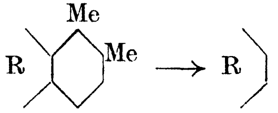
[26] *Ber.*, 1930, **63**, 2997; *A.*, 1931, 242. Compare also K. Warnat, *Ber.*, 1926, **59**, 2388; *A.*, 1926, 1263.

[27] A. Schomer, *Arch. Pharm.*, 1927, **265**, 500; *A.*, 1927, 1097.

[28] G. Hahn and F. Just, *Ber.*, 1932, **65**, 717; *A.*, 760.

[29] G. A. C. Gough and H. King, *J.*, 1931, 2968; *A.*, 68; *Ann. Reports*, 1931, **28**, 166.

When yohimboaic acid is distilled or fused with potassium hydroxide [24] or heated with zinc dust [23] or with lime,[22] it yields a base, $C_{13}H_{12}N_2$, which, like the parent alkaloid, must contain a tertiary N-atom, since it forms a methiodide and according to Winterstein and Walter is accompanied by a second base, $C_{12}H_{10}N_2$. The disposition of the ring systems in these bases is unknown, but it is probably the same as occurs in the products of the action of selenium on yohimbine. When this alkaloid is heated with selenium,[25] it yields three substances: yobyrine, $C_{19}H_{18}N_2$; dihydroyobyrine, $C_{19}H_{20}N_2$; and ketoyobyrine, $C_{20}H_{16}ON_2$. Yobyrine differs from yohimbine by a carbomethoxy-group, a molecule of water and four hydrogen atoms, and ketoyobyrine must be formed by condensation of the carbomethoxy-group with elimination of methyl alcohol and formation of a bridge. On fusion with potassium hydroxide ketoyobyrine yields a basic substance, $C_{11}H_{10}O_2N_2$, and an acid identified as 2 : 3-dimethylbenzoic acid. It has been suggested [25] that this is the benzene nucleus which appears as dimethylindole by other methods of degradation, in which case *o*-oxycarbanil, oxalylanthranilic acid, and indazolecarboxylic acid must arise from a second benzene nucleus with a nitrogen atom adjacent to it. Furthermore the base $C_{13}H_{12}N_2$ (IV), differing from yobyrine, $C_{19}H_{18}N_2$ (V), by C_6H_6, is considered by the same authors to have lost four carbon atoms of the benzene nucleus with the two *o*-methyl groups attached, as is shown below:

(V.)  (IV.)

This benzene nucleus is supposed to be present in yohimbine as a hydroaromatic structure which is dehydrogenated by selenium but degraded by other reagents.

Pyrrole Pigments.[31]

The remarkable progress which has been made in the last 30 years in the elucidation of the structure of blood and leaf pigments is mainly due to the efforts of Nencki, Küster, Piloty, Willstätter, and Hans Fischer and their pupils. The brilliant researches of the last-named were fittingly recognised by the award of the Nobel prize in 1931.

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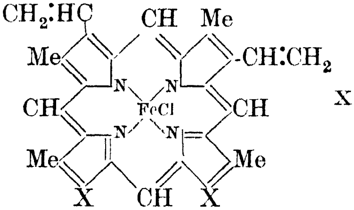
[30] K. Warnat, *Ber.*, 1926, **59**, 2388; *A.*, 1926, 1263.

[31] Valuable summaries by H. Fischer can be found in *ibid.*, 1927, **60**, 2611; *Naturwiss.*, 1930, **18**, 1026; *Nobel Vortrag*, Dec. 11th, 1930.

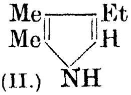
The following account has been written to enable the reader to appreciate the position which has been reached in the chemistry of the blood and bile pigments and also as an introduction to the chlorophyll problem.

Hæmin, obtained from blood by heating with acetic acid and sodium chloride (Teichmann's test), has the constitution (I), as is shown by its properties and by synthesis. It consists of four pyrrole-like nuclei joined in the α-position by methine groups and a peculiar conjugated system of double bonds responsible for the colour. The iron is held in complex combination, since it does not show the ordinary ionic reactions of iron. Inspection of the formula shows how it can give rise to four different hæmopyrrole bases (II—V) by drastic reductive fission with hydriodic acid and also to the four corresponding hæmopyrrolecarboxylic acids (VI—IX).

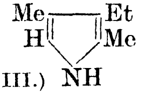
(I.)



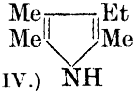
$X = \cdot CH_2 \cdot CH_2 \cdot CO_2H$



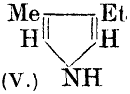
(II.) Hæmopyrrole.



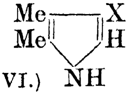
(III.) Cryptopyrrole.



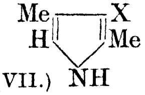
(IV.) Phyllopyrrole.



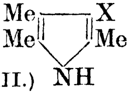
(V.) Opsopyrrole.



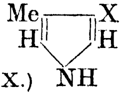
(VI.) Hæmopyrrole-carboxylic acid.



(VII.) Cryptopyrrole-carboxylic acid.



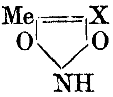
(VIII.) Phyllopyrrole-carboxylic acid.

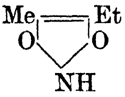


(IX.) Opsopyrrole-carboxylic acid.

On oxidation, the nuclei bearing vinyl groups are completely degraded but the acidic nuclei appear as hæmatic acid (X). If the vinyl groups are converted into ethyl groups by reduction of hæmin with hydriodic acid or catalytically to mesoporphyrin, the hæmatic acid obtained by oxidation is accompanied by methylethylmaleinimide (XI).

(X.)





(XI.)

These reductive and oxidative processes can nowadays be so controlled that they give a clue to the number of nuclei of a given type within the molecule of a pigment. When the iron is removed from hæmin by various reagents, a series of porphyrins is obtained characterised by their fluorescence, dichroism, and the possession of absorption spectra in the visible and the ultra-violet region.[32]

The more important porphyrins derived from hæmin are shown in the following table. In column 3 is shown the number of isomerides obtainable by altering the sequence of groups around the pyrrole rings in the β-position with the condition that each pyrrole nucleus must bear one methyl group, whilst in column 4 is recorded the number of isomerides synthesised to date by H. Fischer and his collaborators.

		Isomerides.		Side Chains.		
		Possible.	Synthesised.			
Hæmin	$C_{34}H_{32}O_4N_4FeCl$	15	2[33]	4Me	2X	$2CH{:}CH_2$
Protoporphyrin	$C_{34}H_{34}O_4N_4$	15	2[33]	4Me	2X	$2CH{:}CH_2$
Hæmatoporphyrin	$C_{34}H_{38}O_6N_4$	15	2[33]	4Me	2X	2CH(OH)Me
Mesoporphyrin	$C_{34}H_{38}O_4N_4$	15	12[34]	4Me	2X	2Et
Ætioporphyrin	$C_{32}H_{38}N_4$	4	4[35]	4Me	—	4Et
Deuteroporphyrin	$C_{30}H_{30}O_4N_4$	15	3[36]	4Me	2X	—
Deuterohæmin	$C_{30}H_{28}O_4N_4FeCl$	15	2[33]	4Me	2X	—

A number of porphyrins have been found to occur naturally in yeast, pearl-oysters, mussels, feathers, egg-shells, and in cases of hæmatoporphyrinuria, and representatives of some of these have been synthesised.

		Isomerides.		Side chains.		
		Possible.	Synthesised.			
Coproporphyrin	$C_{36}H_{38}O_8N_4$	4	4[37]	4Me	—	4X
Conchoporphyrin	$C_{37}H_{38}O_{10}N_4$			4Me	3X	1 succinic acid
Ooporphyrin	$C_{34}H_{34}O_4N_4$	15	2[33]	4Me	2Et	$2CH{:}CH_2$
Uroporphyrin	$C_{40}H_{38}O_{16}N_4$			4Me	—	methylmalonic & succinic acid

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[32] A. Treibs, *Z. physiol. Chem.*, 1932, **212,** 33; W. Hausmann and O. Krumpel, *Biochem. Z.*, 1927, **186,** 203; *A.*, 1927, 893.

[33] H. Fischer and A. Kirstahler, *Annalen*, 1928, **466,** 178; *A.*, 1928, 1385; H. Fischer and L. Nüssler, *ibid.*, 1931, **491,** 162; *A.*, 173.

[34] H. Fischer and co-workers, *ibid.*, 1927, **452,** 289; *A.*, 1927, 469; *ibid.*, **459,** 74; *A.*, 1928, 76; *ibid.*, 1928, **466,** 166; *A.*, 1928, 1384; *ibid.*, 1929, **475,** 274; *A.*, 1929, 1466; *ibid.*, 1930, **480,** 260; *A.*, 1930, 932; *ibid.*, **482,** 211; *A.*, 1931, 101; *ibid.*, **484,** 85; *A.*, 1931, 240.

[35] *Idem*, *ibid.*, 1926, **448,** 186, 201; *A.*, 1927, 962, 963; *ibid.*, **450,** 190; *A.*, 1926, 1261; *ibid.*, 1927, **452,** 285; *A.*, 1927, 469; *ibid.*, **459,** 71; *A.*, 1928, 76; *ibid.*, 1928, **466,** 211; *A.*, 1928, 1382; *ibid.*, 1932, **495,** 26; *A.*, 756.

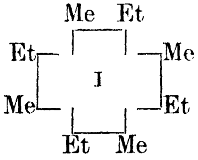
[36] *Idem*, *ibid.*, 1928, **466,** 183; *A.*, 1928, 1385; *ibid.*, 1929, **473,** 245; *A.*, 1929, 1184; *ibid.*, 1931, **491,** 173; *A.*, 173.

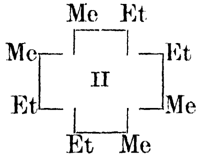
[37] *Idem*, *ibid.*, 1926, **450,** 214; *A.*, 1926, 1261; *ibid.*, 1927, **457,** 97; *A.*, 1927, 1088; *ibid.*, **458,** 132; *A.*, 1927, 1206; *ibid.*, 1928, **461,** 276; *A.*, 1928, 776; *ibid.*, **462,** 249; *A.*, 1928, 902; *ibid.*, **466,** 156; *A.*, 1928, 1384; *Z. physiol. Chem.*, 1929, **182,** 265; *A.*, 1929, 940; *ibid.*, 1931, **196,** 163, 236; *A.*, 1931, 747, 853.

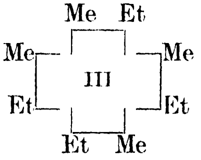
Incidentally a large number of important related porphyrins have been prepared.

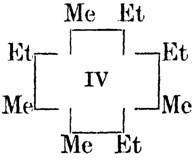
	Isomerides.		Side chains.
	Possible.	Synthesised.	
Porphinmonopropionic acid	8	8[38]	4Me 3Et 1X
Porphintripropionic acid	8	1[39]	4Me 1Et 3X
Tetramethyltetrapropylporphyrin	4	4[40]	4Me 4Pr —
Pyrroporphyrin	24	8[41]	4Me 2Et 1X
Pyrroætioporphyrin	8	8[42]	4Me 3Et —
Deuteroætioporphyrin	15	2[43]	4Me 2Et —
Rhodoporphyrin	24	2[44]	4Me 2Et 1CO$_2$H 1X
*iso*Uroporphyrin	4	2[45]	4Me 4CH(CO$_2$H)$_2$

Ætioporphyrin, $C_{32}H_{38}N_4$, which is obtained indirectly by a pyrogenetic reaction from hæmatoporphyrin, is a fully substituted porphyrin and is a convenient reference substance for all other porphyrins. Four ætioporphyrins are possible which, following the recognised procedure, are shown in abbreviated form as follows, each bracket representing a pyrrole nucleus, since the remainder of the molecules are identical in most porphyrins. All the porphyrins tabulated can be referred to one of these four structures and it is known, for instance, that natural hæmin has its substituents based on ætioporphyrin (III) and so has chlorophyll. If the ethyl groups are replaced by propionic acid groups (X), there will be four possible coproporphyrins, all of which have been synthesised and two of them, coproporphyrins (I) and (III), are identical with naturally occurring coproporphyrins. If, however, only two of the four









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[38] H. Fischer and co-workers, *Annalen*, 1928, **461**, 237; *A.*, 1930, 651; *ibid.*, 1929, **471**, 293; *A.*, 1929, 941; *ibid.*, **475**, 254; *A.*, 1929, 1465; *ibid.*, 1931, **492**, 27, 50; *A.*, 173.

[39] *Idem*, *ibid.*, 1930, **479**, 32; *A.*, 1930, 621.

[40] *Idem*, *ibid.*, 1931, **486**, 20; *A.*, 1931, 746.

[41] *Idem*, *ibid.*, 1929, **473**, 229; *A.*, 1929, 1184; *ibid.*, 1930, 480, 136; *A.*, 1930, 931; *ibid.*, **482**, 199; *A.*, 1931, 101.

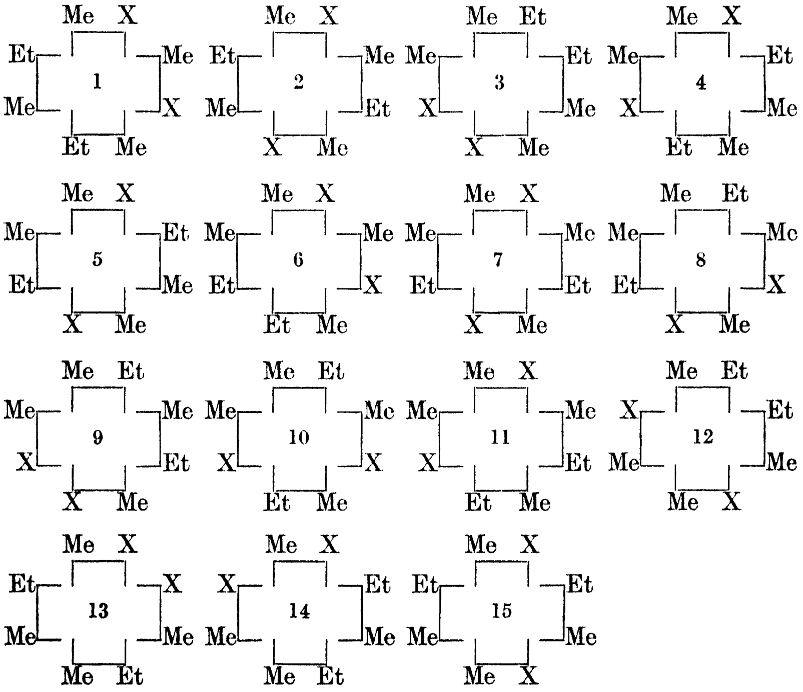
[42] *Idem*, *ibid.*, 1928, **466**, 211; *A.*, 1928, 1382; *ibid.*, 1929, **473**, 243; *A.*, 1929, 1184; *ibid.*, 1930, **480**, 126; *A.*, 1930, 931; *ibid.*, **482**, 199; *A.*, 1931, 101.

[43] *Idem*, *ibid.*, 1928, **466**, 217; *A.*, 1928, 1382; *ibid.*, 1930, **482**, 209; *A.*, 1931, 101; *Z. physiol. Chem.*, 1931, **198**, 56; *A.*, 1931, 967.

[44] *Idem*, *Annalen*, 1929, **473**, 237; *A.*, 1929, 1184; *ibid.*, 1930, **480**, 109; *A.*, 1930, 931.

[45] *Idem*, *ibid.*, 1927, **457**, 91; *A.*, 1927, 1088; *ibid.*, 1930, **483**, 1; *A.*, 1930, 1599; *Z. physiol. Chem.*, 1932, **204**, 68; *A.*, 285.

ethyl groups of ætioporphyrin are replaced by propionic acid groups as in mesoporphyrin, then fifteen mesoporphyrins are possible, 1 and 2 derived from ætioporphyrin (I), 3—5 from ætioporphyrin (II), 6—11 from ætioporphyrin (III), and 12—15 from ætioporphyrin (IV), and of these twelve have been synthesised.



Their dimethyl esters have characteristic melting points and are especially valuable for characterisation, since the decarboxylation products, the ætioporphyrins, have no definite or very high melting points. There are as many hæmins possible as there are mesoporphyrins, since the ethyl groups are replaced by vinyl groups and introduction of iron does not so far as is known increase the number of possible isomerides. Natural hæmin corresponds to mesoporphyrin 9, as will be seen by comparison with the formula for hæmin given at the beginning of the section. The first proof that hæmin had this particular orientation of groups in the β-positions was afforded by the synthesis of mesoporphyrin 9, identical with the product obtained from natural hæmin.[46]

Space does not allow an account of the variety of synthetic methods used by H. Fischer and his collaborators in the preparation of the many porphyrins so far synthesised. Reference can only be made to the representative synthesis of natural hæmin (hæmin IX) and hæmin III corresponding to mesoporphyrins 9 and 3 respectively.

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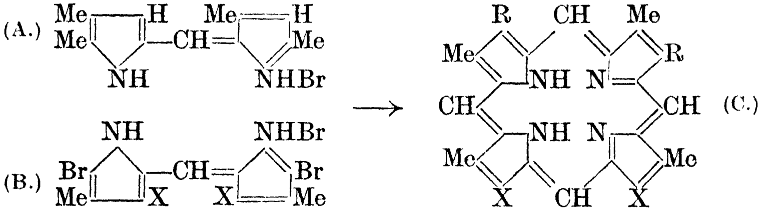
[46] H. Fischer and G. Stangler, *Annalen*, 1927, **459**, 53; *A.*, 1928, 76.

2 : 3-Dimethylpyrrole and 2 : 4-dimethylpyrrole-5-aldehyde were condensed by alcoholic hydrobromic acid to 4 : 5 : 3′ : 5′-tetramethylpyrromethene hydrobromide (A), whilst cryptopyrrolecarboxylic acid (VII, p. 210) on bromination gave 5 : 5′-dibromo-3 : 3′-di-β-carboxyethyl-4 : 4′-dimethylpyrro-2 : 2′-methene hydrobromide (B) [47] with loss of a methylene group. When (A) and (B) were heated in succinic acid at 180—190°, deuteroporphyrin (C; R = H) was obtained.[48]



The latter was converted into deuterohæmin by the action of ferrous acetate, acetic acid, sodium chloride, and hydrochloric acid, since the pyrrole nuclei in the iron complexes are more reactive than in the iron-free porphyrins. On treatment of deuterohæmin with acetic anhydride in presence of stannic chloride, diacetyldeuterohæmin was obtained and it was characterised by conversion into diacetyldeuteroporphyrin (C; R = Ac). On reduction of this porphyrin with alcoholic potassium hydroxide the di-secondary alcohol, hæmatoporphyrin [C; R = CH(OH)Me], was obtained in 24% yield, calculated on the deuterohæmin used. This porphyrin proved to be identical with the natural product obtained from hæmin. It was quantitatively converted by heating in a high vacuum at 105° into protoporphyrin (C; R = $CH{:}CH_2$), which with ferrous iron gave hæmin (p. 210) identical with that obtained from hæmoglobin.

It is a remarkable fact that the structure of hæmin as now determined by synthesis was suggested as early as 1912 by W. Küster,[49] with the same orientation of groups in the β-positions except that a methyl and a vinyl group on one nucleus had to be interchanged. Moreover, it was not until hæmin was synthesised that its constitution was known with certainty, since immediately preceding its synthesis it was still believed to contain one acetylene and one vinyl group.[50]

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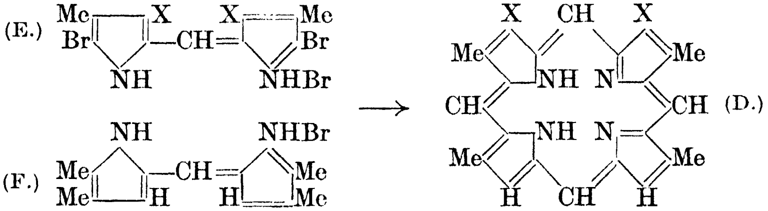
[47] H. Fischer and H. Andersag, *Annalen*, 1927, **458**, 135; *A.*, 1927, 1206.

[48] H. Fischer and A. Kirstahler, *ibid.*, 1928, **466**, 178; *A.*, 1928, 1385.

[49] *Z. physiol. Chem.*, 1913, **82**, 463; *A.*, 1913, i, 210.

More recently H. Fischer and L. Nüssler[51] have synthesised hæmin III with an orientation of groups identical with that suggested by Küster for natural hæmin. The corresponding deuteroporphyrin III (D) was obtained by condensation of 5 : 5′-dibromo-4 : 4′-dimethyl-3 : 3′-di-β-carboxyethylpyrro-2 : 2′-methene hydrobromide (E) and 4 : 5 : 4′ : 5′-tetramethylpyrro-2 : 2′-methene hydrobromide (F).



The subsequent steps were then on the same lines as for the synthesis of natural hæmin IX.

All authors are agreed that in hæmin the iron is in the tervalent state and on its reduction to the bivalent state a hæmochromogen is obtained accompanied by a change in the spectrum and a decrease in stability. Hitherto hæmochromogen was always stabilised by formation of complexes with nitrogenous bases such as nicotine, pyridine, and hydrazine, but it has now proved possible to isolate the hæms or complex salts with bivalent iron but without nitrogenous addenda.[52] Thus, if suitable porphyrins are treated in nitrogen with a ferrous salt, crystalline hæms are obtained. This has been found possible for proto-, ætio- and meso-porphyrins and their esters and the products on addition of pyridine give intense hæmochromogen spectra. Hæmoglobin is a molecular compound of hæm and globin, but it is exceptional in that it has no hæmochromogen spectrum. In this connexion it is of interest that hæmatin (hæm-oxide) can form additive products with glyoxaline, methylglyoxaline, and pilocarpine.[53] The additive product with two molecular proportions of glyoxaline separates unchanged from pyridine solution and does not part with its glyoxaline even at 100°. Glyoxaline has thus the greatest affinity for hæmatin and since hæmatin and globin combine to give methæmoglobin,[54] the suggestion is made [53] that the combination is through the glyoxaline nuclei of histidine, the characteristic amino-acid of globin.

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[50] H. Fischer and G. Stangler, *Annalen*, 1927, **459**, 53; *A.*, 1928, 76.

[51] *Ibid.*, 1931, **491**, 162; *A.*, 173.

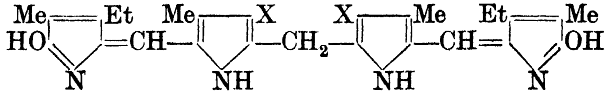
[52] H. Fischer, A. Treibs, and K. Zeile, *Z. physiol. Chem.*, 1931, **195**, 1; *A.*, 1931, 633.

[53] W. Langenbeck, *Ber.*, 1932, **65**, 842; *A.*, 757.

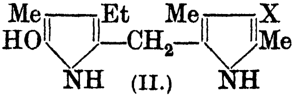
[54] R. Hill and H. F. Holden, *Biochem. J.*, 1926, **20**, 1326; *A.*, 1927, 67.

Bile Pigments.—Bilirubin, $C_{33}H_{36}O_6N_4$, is a bile pigment which is supposed to arise from the break-down of hæmoglobin in cells of the reticulo-endothelial system, especially those of the liver. It is a rare substance difficult to obtain, the best source being ox gall-stones. It differs from hæmin by having one carbon less, two oxygen atoms more, and no iron. It has no characteristic absorption spectrum, so the porphyrin ring-system is probably absent. It is characterised by striking colour reactions, of which Gmelin's is the most important. This may be carried out by carefully adding nitric acid containing nitrite to a solution of the pigment in chloroform. The latter passes through the colour changes green, blue, violet, red, and finally yellow.[55] On energetic oxidation with chromic acid bilirubin gives hæmatic acid [56] (X, p. 210) and on energetic reduction with hydriodic acid, cryptopyrrole (III, p. 210) and cryptopyrrolecarboxylic acid [57] (VII, p. 210).

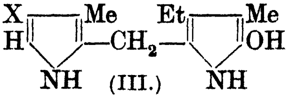
The most important derivatives are those obtained by gentle reduction. Sodium amalgam or catalytic reduction yields mesobilirubin, $C_{33}H_{40}O_6N_4$; this on further reduction yields mesobilirubinogen (urobilinogen), which gives an intense colour reaction with Ehrlich's *p*-dimethylaminobenzaldehyde reagent. Mesobilirubin on oxidation gives hæmatic acid (X, p. 210) and methylethylmaleinimide (XI, p. 210) just as mesoporphyrin does. On reduction with hydriodic acid and acetic acid mesobilirubin yields a mixture of two acids which differ from each other in composition by a methylene group : bilirubic acid, $C_{17}H_{24}O_3N_2$, and *neo*bilirubic acid, $C_{16}H_{22}O_3N_2$, both of which on further reduction give rise to cryptopyrrole (III, p. 210). The acidic reduction products are, however, different, for bilirubic acid gives cryptopyrrolecarboxylic acid (VII, p. 210) whilst *neo*bilirubic acid gives hæmopyrrolecarboxylic acid (VI, p. 210). These observations receive a ready explanation on the formulæ (I) for mesobilirubin, (II) for bilirubic acid, and (III) for *neo*bilirubic acid.[55]



(I).



(II.)



(III.)

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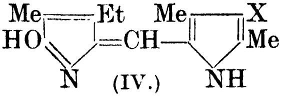
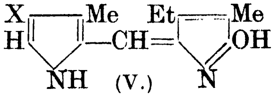
[55] H. Fischer and R. Hess, *Z. physiol. Chem.*, 1931, **194**, 201; *A.*, 1931, 497.

[56] W. Küster, *ibid.*, 1898, **26**, 314; *A.*, 1899, 314.

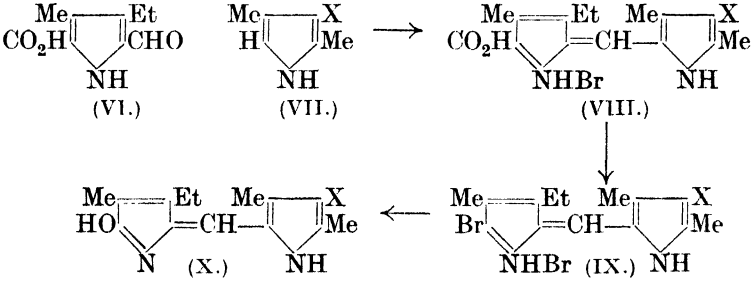
[57] H. Fischer and E. Adler, *ibid.*, 1931, **197**, 237; *A.*, 1931, 967.

These two acids (II) and (III) are the leuco-compounds corresponding to xanthobilirubic acid (IV) and *neo*xanthobilirubic acid (V), into which they are respectively converted by the action of sodium methoxide [58] or potassium methoxide.[55]


(IV.)


(V.)

Conversely, *neo*xanthobilirubic acid (V) is converted by condensation with formaldehyde into mesobilirubin (I), which gives the Gmelin reaction and is identical with the product obtained from bilirubin. This incidentally supports the symmetrical structure assigned to mesobilirubin, and mesobilirubinogen will be the corresponding trimethane derivative. The orientation of the groups attached to the pyrrole nuclei follows from the synthesis of xanthobilirubic and *neo*xanthobilirubic acids. 5-Aldehydo-3-methyl-4-ethylpyrrole-2-carboxylic acid (VI) and cryptopyrrolecarboxylic acid (VII) condense in presence of a large excess of hydrobromic acid to give 5-carboxy-4 : 3′ : 5′-trimethyl-3-ethylpyrromethene-4′-propionic acid hydrobromide (VIII), which on bromination gives 5-bromo-4 : 3′ : 5′-trimethyl-3-ethylpyrromethene-4′-propionic acid hydrobromide [59] (IX). The latter on treatment with potassium or silver acetate yields xanthobilirubic acid (X) identical with the product from natural sources.


(VI.) (VII.) (VIII.) (IX.) (X.)

Three isomerides of xanthobilirubic acid are possible and all were synthesised by suitable methods. When xanthobilirubic acid was brominated, it gave an unstable substance which on treatment with pyridine passed into mesobilirubin identical with that from natural bilirubin.[60] During this synthesis one carbon atom is lost (the ethanes are unstable), for which there are many analogies in the syntheses of dipyrromethanes from methylbrominated pyrroles.[61] Since mesobilirubin on reduction with hydriodic acid gives *neo* bilirubic acid or by fusion with resorcinol gives *neo*xanthobilirubic acid, the synthesis of xanthobilirubic acid is also a synthesis of *neo*xanthobilirubic acid. In a similar manner bromination of the isomeric mesobilirubic acids gave isomeric mesobilirubins, all of which are important, since there is some evidence that more than one bilirubin occurs in nature.

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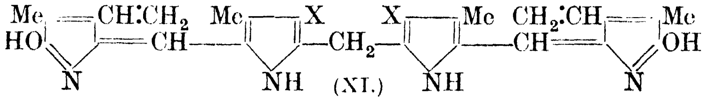
[58] H. Fischer and H. Rose, *Ber.*, 1913, **46**, 439; *A.*, 1913, i, 382.

[59] H. Fischer and H. Berg, *Annalen*, 1930, **482**, 189; *A.*, 1931, 101.

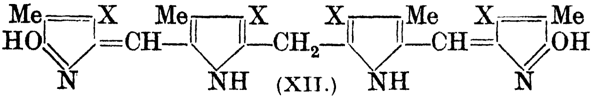
[60] H. Fischer and E. Adler, *Z. physiol. Chem.*, 1931, **200** 209; *A.*, 1931, 1420.

On the basis of the results recorded above, the most probable formula for bilirubin is (XI).


(XI.)

Such a structure has an orientation of groups in the β-positions corresponding to a mesoporphyrin 13 (p. 213) or an ætioporphyrin IV (p. 212), which has no other natural representative. It follows from this that the conversion of hæmoglobin into bilirubin must involve intermediate degradation to pyrrole units. Against the above structure for bilirubin is the observation that on oxidation with nitrous acid a substance is formed which has a composition, $C_7H_7O_2N$, agreeing with that of methylvinylmaleinimide, but on catalytic reduction takes up two hydrogen atoms to give a substance which is not methylethylmaleinimide. Formulæ have been suggested for these substances containing fused pyrrofuran rings produced by ring-formation between the vinyl group and an α-hydroxyl group, but this is difficult to reconcile with the relative orientation of the vinyl and hydroxyl groups necessitated by (XI). The final decision will no doubt depend on a synthesis of the structure (XI).

The nomenclature of the porphyrin group is applicable to the bilirubin group. If the vinyl groups in (XI) are replaced by propionic acid (X) groups, a coprobilirubin which may occur naturally in certain pathological conditions is produced corresponding to ætioporphyrin IV and such a coprobilirubin (XII) has been synthesised.[62]


(XII.)

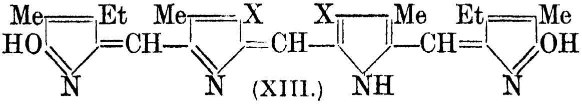
If the vinyl and propionic acid groups are replaced by ethyl groups, an ætiomesobilirubin or decarboxylated mesobilirubin is produced, of which one example has also been synthesised.[63]

[61] H. Fischer and P. Halbig, *Annalen*, 1926, **447**, 123; *A.*, 1926, 621.

[62] H. Fischer and E. Adler, *Z. physiol. Chem.*, 1932, **210**, 139; *A.*, 1045.

[63] H. Fischer and E. Adler, *ibid.*, 1932, **206**, 187; *A.*, 627.

When mesobilirubin (I) is oxidised with ferric chloride, a ferrichloride of a new pigment, ferrobilin, is obtained,[64] which by the action of alkali gives glaucobilin (XIII). The particular orientation of pyrrole linkages ascribed to it follows from its synthesis by the action of formic acid on *neo*xanthobilirubic acid (V).



(XIII.)

The vinyl analogue of this substance in which the ethyl groups are replaced by vinyl groups has now been found in nature,[65] but a true pyrrole structure is preferred for a terminal nucleus rather than for one of the central nuclei as shown in (XIII). This substance occurs as uteroverdin in the dog's placenta, as a constituent of the pigments of birds eggs (sea-gulls eggs gave 250 mg. from 5 kg. of shells), and as a by-product in the extraction of bilirubin from ox gall-stones. It has also been obtained artificially by oxidation of bilirubin with ferric chloride and is hence called dehydrobilirubin. The constitution assigned is supported by the results of reductive fission—formation of bilirubic acid—and oxidation—formation of methylethylmaleinimide after preliminary reduction but not before.

Harold King.

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[64] H. Fischer, H. Baumgartner, and R. Hess, *Z. physiol. Chem.*, 1932, **206**, 201; *A.*, 627.

[65] R. Lemberg, *Annalen*, 1931, **488**, 74; *A.*, 1931, 1066; R. Lemberg and J. Barcroft, *Proc. Roy. Soc.*, 1932, [*B*], **110**, 362; *A.*, 627; R. Lemberg, *Annalen*, 1932, **499**, 25.

ANALYTICAL CHEMISTRY

In the period under review there is little new material of outstanding importance. The most interesting work in analytical chemistry has dealt with the detailed investigation of known processes and with the perfection of details and apparatus in such modern processes as electrometric determinations. The following discussion will be devoted mainly to considering some of the more important subjects investigated.

Quantitative Separation of Hydroxides.—The separation of metals by precipitation as hydroxide is usually incomplete owing to co-precipitation or adsorption of other metal radicals, to the colloidal character of the precipitates in their initial stages, to the fact that the hydroxides can only be precipitated when a particular p_H is attained, depending upon the metal, and also in part owing to the precipitation of more or less basic salt which is hydrolysed very slowly. The range of p_H for precipitation of the hydroxides is considerable, in some cases being below 4. A full discussion of the mechanism of hydroxide precipitation has been given by H. T. S. Britton.[1]

It is a matter of experience that the separation is more complete the denser the precipitate of hydroxide. Of the substances tried by us, hydroxylamine is found to be helpful in decreasing the gelatinous character of some hydroxides, *e.g.*, chromium hydroxide precipitated by ammonia. A promising method is described by F. L. Hahn[2] in which a mixture of sodium azide and sodium nitrite in dilute solution is added to a faintly acid solution of iron, aluminium, or chromium. This reagent is effective in separating this group of metals from large admixtures with the nickel group. The precipitate forms quickly and is easily separated by filtration. A double precipitation will, for example, give a complete separation of iron from manganese. This method of precipitation does not introduce into the substances under test any foreign metallic radical, in contradistinction to the older barium carbonate process. Frequently, however, the addition of another metal is of no importance, and precipitation of the iron group of metals, by means of zinc oxide, for example, has the advantage of rapidity. The use of zinc oxide is not new, but the conditions for completeness of separation, particularly as applied to the analysis of alloy steels, have now been carefully investigated.[3] Britton has shown that zinc hydroxide begins to precipitate at p_H 5·2, iron and aluminium at lower p_H, cobalt, manganese, and bivalent metals generally at higher p_H. On this basis a separation might be expected, and it is found that the zinc oxide method can be successfully applied to the separation of iron, tungsten, vanadium, chromium, uranium, aluminium, and titanium from cobalt, manganese, and nickel in the analysis of steel. Although the separation of cobalt and manganese is easily effected and is complete, nickel cannot be so readily separated despite the fact that the p_H for initial precipitation of these metals is nearly the same. On the other hand, tervalent chromium is completely precipitated by zinc oxide, although the initial p_H for precipitation is very close to that of zinc. While the foregoing method for determination of cobalt in materials containing iron is accurate, it is nowadays common to require determinations of cobalt in much larger proportions than formerly in high-speed or magnet steel containing vanadium, tungsten, and chromium, amongst other metals of the alloy. The elimination of iron in such cases by the older methods is lengthy and tedious, but may be effected more readily by a modification of the process of extraction of ferric chloride from its solution in hydrochloric acid by means of ether, followed by the removal of chromium, tungsten, and vanadium by treatment with sodium peroxide and sodium hydroxide. Traces of copper and iron may be separated by "cupferron," leaving a cobalt solution ready for precipitation with α-nitroso-β-naphthol.[4] The process here outlined briefly is more rapid and certain than methods hitherto described in which the cupferron was not utilised to eliminate the last of the iron, and it is rendered possible because this reagent does not interfere with the subsequent precipitation of cobalt by the naphthol derivative.

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[1] "Hydrogen Ions," Chap. 15.

[2] *Ber.*, 1932, **65**, [*B*], 64; *A.*, 244.

Determination of Boron.—The increasing importance of a knowledge of the minute quantities of boron in water and natural products is doubtless the reason for a number of papers dealing with the method of detecting and estimating this element. There is no great difficulty in determining boron even in very small quantities when a solution is obtained in a condition suitable for the estimation, but it is just this preliminary preparation which is not easy to carry out, and the purpose of most of the investigations is to obtain a suitable final solution and avoid loss of boron during its preparation and subsequent treatment. Some natural waters contain 0·4 mg. of boron per litre and upwards, and it has been found possible to determine these small quantities, either in the water directly, or after concentration to a small volume with a little added alkali. At p_H 7·6 boric acid is only neutralised to the extent of about 12% but if enough mannitol is present it may be completely neutralised at this p_H. Since other weak acids or bases are not in general affected by mannitol, it becomes possible to determine boric acid by bringing the solution to p_H 7·6 with sodium hydroxide either potentiometrically or by means of phenol-red as indicator. As a matter of fact, if larger amounts of mannitol are used, the end point may be much lower than p_H 7·6, and this procedure lowers the amount of boric acid neutralised before mannitol is added.[5]

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[3] J. I. Hoffman, *Bur. Stand. J. Res.*, 1931, **7**, 883; *A.*, 137.

[4] *Idem, ibid.*, 1932, **8**, 658; *B.*, 728.

The determinations of boron in plant and animal tissues are not at all so readily made as in the foregoing process, for the destruction of organic matter, necessarily carried out as the first stage, leads to serious loss if at any point acidity is developed during heating. If the initial preparation is carried out by maintaining an alkaline condition during ashing of the material, it is possible, by impregnating turmeric-stained flax threads, to determine with some accuracy as little as 0·01 γ of boron, but the test may be to some extent vitiated by the presence of large quantities of salts in the ash under examination. For this reason it is usually preferable to distil the acidified ash with methyl alcohol, thus volatilising the boron. The subsequent treatment of the methyl borate depends on the quantity present. For large quantities, such as may be found in artificial borosilicates, we have trapped the borate in sodium tungstate for gravimetric determination, or in aqueous sodium hydroxide for subsequent volumetric determination in the presence of mannitol. The choice of acid for catalysing the reaction between boric acid and the alcohol needs consideration in each case examined. Usually sulphuric acid is used and the distillation is arranged so that the acid–alcohol mixture loses most of its water, but not all, which is usually secured by passing in the vapour of fresh methyl alcohol at nearly the same rate as that lost by distillation. For silicates, much larger amounts of alcohol and acid are required, and the water present must be regulated in order to prevent separation of silica, which adsorbs boric acid should the silica separate in a gelatinous state.[6] Phosphoric acid can likewise be employed in place of sulphuric acid, but very careful attention is then necessary to keep too much water from distilling away, otherwise we have found phosphoric esters to distil over with the borate, adding considerably to the difficulty of the final determination of the boron even in large amounts.

When plant ashes have been suitably treated, the neat and promising procedure recently developed for determining the boron spectroscopically is to be borne in mind.[7] The ashes are acidified with citric acid and the boron is distilled out with methyl alcohol containing 5% of phosphoric acid. The methyl alcohol–methyl borate mixture is burnt in oxygen in a special form of burner under specified conditions; the flame is observed with a direct-vision spectroscope through a glass cell containing 50 ml. of water into which is dropped $0{\cdot}01N$-potassium permanganate until the most intense green boron band in the spectrum of the flame is absorbed. A calibration curve is drawn showing ml. of $0{\cdot}01N$-potassium permanganate against mg. of boron. The recorded data indicate that the method is capable of furnishing satisfactory determinations.

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[5] F. J. Foote, *Ind. Eng. Chem.* (*Anal.*), 1932, **4**, 39; *A.*, 242.

[6] E. Schulek and G. Vastagh, *Z. anal. Chem.*, 1932, **87**, 165; *A.*, 354.

Sometimes it is necessary to determine both fluorine and boron in organic substances, and the difficulty then arises of eliminating the carbon and preparing a residue suitable for these determinations. This problem has been examined afresh [8] with some measure of success for the comparatively simple substances chosen for testing the method. Briefly the essential part of the process is the combustion of the substance in a Parr bomb with a mixture of sodium peroxide, potassium chlorate, and sucrose, first enclosing the material in a gelatin capsule in order to keep it away from the oxidising mixture which would otherwise attack the organic boron trifluorides with violence. The alkali is removed by boiling the liquid washed from the bomb with ammonium chloride, and the fluorine is then precipitated by means of calcium nitrate. In the special method of treatment of the calcium fluoride by limited washing, it is indicated that a solubility correction for this salt is avoided. The boron in the filtrate from the precipitated fluoride is determined in the usual way with mannitol. The results given for three compounds are very close to the calculated values.

Conductometric Titrations.—In view of the fact that most chemists have made measurements of the conductivity of solutions, it is somewhat surprising that the method is not used in practice as frequently as it deserves. It is at least as accurate as the ordinary titration relying upon indicators, and much more so if the apparatus is chosen properly. Further, it can be employed where potentiometric methods fail, for example, in the titration of weak acids or bases when proper account is taken of the varying slopes of the conductivity curves before and after the equivalence or neutralisation point is reached. The titration of strong acids and bases when coloured impurities or the natural colour of the liquid precludes the use of indicators, is effectively carried out conductometrically, for it is not necessary to know the absolute conductivity of the liquid, the reciprocal of the resistance being sufficient for the purpose, if plotted against volume of the titration liquid. A simple form of apparatus has been described for use with such liquids.[9] The difficult titration of a weak acid by a weak base which must sometimes be undertaken can be made conductometrically in many cases, for the electrolyte produced as soon as titration is begun is, as a rule, sufficiently strongly ionised to give a large increase in conductivity up to the point of equivalence, after which further addition of titrating liquid produces very little change in conductivity. In this case the " neutral " point of intersection is found by producing the curve (usually a straight line as titration progresses) for the initial increase of conductivity and the final stationary curve. Cases often arise where a titration, whether a neutralisation or a precipitation process, must be conducted in the presence of alcohol; the neutral salts produced during a titration in aqueous alcoholic solutions do not alter the "neutral" point, but the curves in the neighbourhood of equivalence gradually merge into each other on both sides of the equivalence point. These effects have been further studied and corrections applied for the titrations.[10] A closely allied matter is the shifting of the end-point of the titration of a weak acid with sodium hydroxide in alcoholic solutions, as the proportion of alcohol increases. This is, of course, of the greatest importance in determining free fatty acids in glycerides, where alcohol is commonly used. For accurate work, corrections must be applied to the values obtained on titration; naphtholphthalein is a better indicator for the purpose than either phenol- or thymol-phthalein.

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[7] J. S. McHargue and R. K. Calfee, *Ind. Eng. Chem.* (*Anal.*), 1932, **4**, 385; *A.*, 1221.

[8] D. J. Pflaum and H. H. Wenzke, *ibid.*, p. 392; *A.*, 1269.

Of the practical applications of conductometric titrations, an important development is the titration of small quantities of fatty acids by means of a solution of sodium hydroxide in methyl alcohol. An alcoholic solution of the fatty acid is obtained in a special extraction apparatus, and to the solution is added a small quantity of hydrochloric acid, whereby a conducting solution results. On titration with the sodium hydroxide, the conductivity curve, as measured by galvanometer deflexions with a "thermo-cross" apparatus, is found to consist of three straight lines. The first is the diminution of conductivity due to neutralisation of the small added quantity of hydrochloric acid, the second is the slowly increasing conductivity due to the neutralisation of the fatty acid, and the third arises from the greatly increased rate of rise of conductivity due to the excess of sodium hydroxide. The projection of the second line on the abscissa (representing volume of sodium hydroxide added) gives the quantity of reagent required for neutralisation of the fatty acid.[11] Owing to the small dissociation of the fatty acid and the use of an aqueous-alcoholic medium, it seems very likely that errors arising from shifts of the equivalence points are largely eliminated in the conditions of test.

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[9] T. Callan and S. Horrobin, *J. Soc. Chem. Ind.*, 1928, **47**, 329T; *B.*, 1929, 154.

[10] W. Poethke, *Z. anal. Chem.*, 1931, **86**, 399; *A.*, 135.

An unusual application of the conductometric method is the titration, in an atmosphere of nitrogen, of tetra*iso*amylammonium iodide dissolved in diethylzinc with ethylsodium in the same solvent.[12] It was observed, by following the course of titration, that the conductivity reached a minimum when equimolecular quantities had reacted, the suggestion being that ethyltetra*iso*amylammonium, $N(C_2H_5)(C_5H_{11})_4$, had been formed.

Colorimetric Measurements and "Boundary Layer" Photoelectric Cells.—In using colorimeters which depend upon comparison of different thicknesses of coloured liquids, as, for example, the modern forms of the Duboscq colorimeter, the errors arising from different intensities of the coloured solutions, peculiarities of the right and left eyes, and fatigue are often ignored. Even when the two solutions to be compared are interchanged, divergencies exceeding 1 mm. in height may be obtained. In any general considerations of the best method of using colorimeters, certain factors must be recognised, especially, on the one hand, that the observer's eyes must be "trained," and on the other, that they become fatigued very rapidly. Even in an observation lasting less than ten seconds the eye passes through the three stages, of increasing, maximum, and diminishing delicacy of power of matching two coloured solutions. Before repeating the observation, at least five seconds are necessary for the eye to recover its initial power. With the object of diminishing errors due to this rapid fatigue of the eye, a detailed investigation of the best conditions has been made and rules for the greatest accuracy are laid down.[13] The ordinary method of keeping the eye at the eyepiece while adjusting the height of the standard coloured liquid is given up, since it involves a time of observation which brings the eye into the period of fatigue. The procedure recommended is to make a match of colour by varying the height of liquid in the ordinary way, as an approximate measure of the height. A slight variation in height of the standard liquid is then made and an observation is carried out rapidly (about 3 seconds) before the eye has time to tire. These rapid observations are repeated with slightly different heights above and below the match points and tabulated. In this way it is possible to ascertain the position of matching to 0·2 mm. Certain general considerations are worthy of note for accurate work. For each coloured substance there are certain concentrations and depths of liquid which give the best results. For example, in Denigès's method [14] for determining phosphoric oxide by formation of molybdenum-blue, the closest results are obtained with a concentration of 1·5—2·5 mg. of P_2O_5 per litre. It is also to be observed that better results are found by using one eye, in preference to both eyes alternately.

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[11] G. Jander and K. F. Weitendorf, *Angew. Chem.*, 1932, **45**, 705.

[12] F. Hein and H. Pauling, *Z. Elektrochem.*, 1932, **38**, 25; *A.*, 243.

[13] N. E. Pestov, *Z. anal. Chem.*, 1932, **89**, 9; *A.*, 920.

Improvements in photoelectric cells, and especially the development of cells of maximum sensitivity for different parts of the spectrum, point the way to developments in colorimetric determinations which should replace the " normal " eye. In this field the recent developments of the boundary-type cells such as the cuprous oxide or the selenium–chromium type offer advantages in facility of use, and rapidity and robustness of apparatus. For this kind of cell no external batteries are required. The lay-out is simple : a constant source of light, a good condensing lens, and a galvanometer or micro-ammeter according to the method of use decided upon.[15] It is desirable to select a coloured screen, *e.g.*, special green glass, so that a fairly narrow band is cut out of the white light for projection through the test liquid on to the photo-cell. Mr. L. G. Groves and one of the authors [16] have for some time used a cuprous oxide cell covered with a thin film of gold for which the maximum sensitivity to light of colour temperature about 2800° Abs. is in the green region of the spectrum. Such a cell shows a comparatively large change in current for a small change in colour in the region green–yellow, towards either red or blue, and is excellent for titrations with bromocresol-green or methyl-red indicators. Since the response of the photo-cell is very rapid—much less than 10^{-3} second—the use of the cell for measuring the depth of colour produced by vitamin *A* with antimony trichloride is indicated. Usually this is determined by means of Lovibond tintometer glass units and an endeavour is made to read maximum intensity. With the cuprous oxide cell we find that readings can be taken immediately after mixing and the rate of variation of the transmitted light can be followed readily with a fairly delicate micro-ammeter. The curve of growth and decay of colour can then be observed continuously.

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[14] *Compt. rend.*, 1927, **185**, 777; *A.*, 1927, 1156; 1928, **186**, 1052; *B.*, 1928, 420.

[15] R. H. Muller, *Mikrochem.*, 1932, **11**, 353; *A.*, 1012; H. M. Partridge, *Ind. Eng. Chem.* (*Anal.*), 1932, **4**, 315; *A.*, 924.

[16] Unpublished work.

A further extension for continuous recording purposes is obvious, since the current produced by illumination is ample for application to a recording galvanometer of the type made by the Cambridge Instrument Company.

Fluorescence Methods of Analysis.—The appearance of a full summary of the methods of application of fluorescence [17] to the detection or characterisation of various substances is opportune in view of the far-reaching claims sometimes made for this method of test. Perusal of this paper shows that the correct interpretation of the fluorescence observed is by no means simple, unless the material under test is known and the operator is experienced. The apparatus required is simple : a source of ultra-violet light, *e.g.*, a mercury-vapour lamp or metallic arc, an " ultra-violet glass " filter such as Wood's ultra-violet glass, which transmits a large proportion of radiation from about 2800 to 4000 Å., and a box to hold the source of radiation behind the glass screen. The quantitative utilisation of fluorescence has not yet advanced very far, one difficulty arising from the circumstance that measurement of the intensity of fluorescence is a matter of individual experience. Despite this, some progress has been made and a few of the results are interesting. The use of the fluorescent " stick " of J. Eisenbrand [18] is capable of extension. Briefly, this consists in dipping part of a closed tube of some fluorescent material, say quinine sulphate solution, into the liquid under examination. If the liquid absorbs ultra-violet light, then the part of the stick inside the liquid becomes darker than that outside and may even become invisible, so that a promising method of evaluating the concentration of fluorescent liquids is indicated. Many attempts have been made to measure the intensity of the fluorescent radiation, some methods depending upon examination of the scattered light as in nephelometric observations, some upon photometric wedges, and one utilising the standard Guild Colorimeter whereby the content of red, blue, and green light of the fluorescent substance may be reconstituted on a purely physical basis.[19]

Discussion has arisen on the subject of the most suitable concentration for quantitative work in fluorescent liquids, and it has been suggested that a maximum fluorescence occurs at a particular concentration. The fact seems to be that there is an optimum condition depending upon the mutual effect of absorption of the incident ultra-violet light by the liquid and the resulting fluorescence, and that if a thin enough layer is observed the interference is so diminished that the fluorescence can be examined to best advantage. This further indicates that quantitative results will be obtained best with the more dilute solutions. Apart from this physical condition, the p_H of the fluorescent liquid has a large effect on the intensity of fluorescence. Within as little as 0·2 unit of p_H as much as 70% variation in fluorescence has been observed with naphtholsulphonic acids.[20] From this fact a necessary precaution is to employ water buffered to the same p_H as the fluorescent solution for diluting test liquids.

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[17] M. Haitinger, *Mikrochem.*, 1932, **11**, 429; cf. P. W. Danckwortt, "Die Lumineszenz-Analyse im filtrierten ultravioletten Licht," Leipzig, 1929.

[18] *Z. angew. Chem.*, 1929, **42**, 445; *A.*, 1929, 666.

[19] G. E. Trease, *Pharm. J.*, 1930, **124**, 264.

In all attempts to use the fluorescence arising from the incident ultra-violet light as a quantitative method, it has to be remembered that the fluorescence may change owing to photochemical effects purely, or to the combined effect of light and oxygen. The fading of the red fluorescence of porphyrin through oxidation is an example of this; [21] the general oxidation occurring during fluorescence with dyestuffs such as eosin and rhodamine, and natural substances like vegetable oils, æsculin, and phloxin, is a subject which has attracted attention from its bearing on the physical condition of these materials.[22]

The change of fluorescence with p_H is now an established means of determining by titration very minute quantities of acids or bases with the aid of ultra-violet light, in many cases with coloured or turbid liquids. While Boyle knew nothing of p_H values—and might conceivably have declined to apply the terminology if he had known—he used an infusion of *lignum nephriticum* to test for alkalinity and acidity. However, it is satisfactory to note that the method of using change, or suppression, of fluorescence for indicator purposes is extending. The important observation of J. Eisenbrand [23] that quinine has two ranges of inflexion, one at p_H 6 and the other at p_H 9·5—10, has been utilised by him quantitatively. Strong acids are indicated very sharply, even in very dilute solutions at p_H 6, whereas weak acids which at first show blue-violet fluorescence, give no colour at p_H 9·5. A full range of this class of indicator depending upon fluorescence in ultra-violet light is now available. For example, eosin can be used to p_H 3, by its green fluorescence; salicylic acid changes from colourless to dark-blue at p_H 3; umbelliferone is especially delicate, changing from colourless to blue in the range p_H 6·5—7·6.[24]

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[20] L. J. Desha, R. E. Sherill, and L. M. Harrison, *J. Amer. Chem. Soc.*, 1926, **48**, 1493; *A.*, 1926, 996.

[21] S. Rafalowski, *Z. Physik*, 1931, **71**, 798; *A.*, 1931, 1212.

[22] R. W. Wood, *Phil. Mag.*, 1922, [vi], **43**, 757; J. C. McLennan, *Proc. Roy. Soc.*, 1923, [*A*], **102**, 256.

[23] *Pharm. Z.*, 1929, **74**, 249; *A.*, 1929, 528.

A few applications of fluorescence or ultra-violet colorimetry to the detection of elements will serve to illustrate the extraordinary utility of this field of investigation. Traces of uranium can be found by the yellow fluorescence produced on fusion of the substance under examination with sodium fluoride, thus giving a good method for use with animal tissues and plant structures. The detection of arsenic with mercury bromide papers in quantities less than 0·001 γ by ultra-violet light is now so well established that it is nearly impossible to obtain reagents which will not give positive indications in these conditions. More recently determinations of cadmium in concentrations of the order of 1 in 2,500,000 have been carried out, and the details for accuracy defined.[25] In very dilute solution it is difficult to see cadmium sulphide, and in any case the colour of this sulphide is not suitable for accurate colorimetric use in the ordinary way; but in ultra-violet light the colour comes out with great distinctness. To apply the method to organic substances, the material is oxidised by means of a mixture of sulphuric acid and nitric acid, as in the Kjeldahl process, and the sulphide is precipitated from the resulting solution after suitable treatment in a prescribed manner.

Inorganic Analysis.

Organic reagents have been applied to inorganic analytical operations for a very long period and several now rank among the classical methods; of these may be cited oxalates, tartrates, and dimethylglyoxime. One of the most interesting developments in the analytical field during the past 10 years or so has been the extension of the application of such substances, and while much of the work has been carried out on new additions to this class of reagent, the older ones have not been neglected. Broadly, these compounds may be divided into three sections : indicators, reagents for colorimetric tests, and those forming insoluble complex compounds with metals. Of these, the last are often particularly adapted to microanalysis on account of their high molecular weight and corresponding low content of the metal.

The following account, by no means exhaustive, is intended to summarise briefly the possibilities of some of these compounds.

Salicylaldoxime, which is readily prepared from the aldehyde, was proposed by F. Ephraim [26] as a precipitant for copper from a slightly acetic solution, and separations from various metals were effected though O. L. Brady [27] found that under the prescribed conditions of acidity, some nickel was also precipitated. In the presence of ferric iron, precipitation is best effected in very dilute hydrochloric solution,[28] or in the presence of tartrate.[29] D. G. Ives and H. L. Riley [30] used this method to determine the copper in its salts with certain alkylmalonic acids. The oximes of various other phenolic aldehydes can also serve to precipitate copper,[31] but possess no advantage over salicylaldoxime. F. Feigl and A. Bondi [32] have investigated the atomic grouping which seems to be more or less specific for copper.

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[24] Y. Volmar and E. Widder, *Bull. Soc. chim.*, 1929, **45**, 130.

[25] L. F. Fairhall and L. Prodan, *J. Amer. Chem. Soc.*, 1931, **53**, 1321; *A.*, 1931, 701.

[26] *Ber.*, 1930, **63**, [*B*], 1928; *A.*, 1930, 1393.

Benzoinoxime is another precipitant for copper, though E. Azzalin [33] found that it was less satisfactory in the presence of other metals than was first indicated.[34] For copper, it is certainly inferior to salicylaldoxime, but H. B. Knowles [35] has shown that molybdates are completely precipitated by it from quite strongly acid solutions; provided vanadates and chromates are first reduced, tungstates are practically the only interfering salts and this can readily be allowed for by precipitation with cinchonine from a solution of the mixed ignited and weighed oxides.

Dimethylglyoxime gives a pink coloration with ferrous salts on addition of ammonia [36] which has been applied to the detection of vanadium.[37] The colour is transient owing to the readiness with which alkaline ferrous solutions tend to oxidise, but can be preserved by covering the solution with ligroin. In connexion with the better-known use of this reagent for nickel, it may be recorded that the precipitate can be prepared for weighing by washing with alcohol and ether,[38] which, though it has been disputed, would appear to be satisfactory provided an adequate current of air is finally drawn through the crucible;[39] precipitation in the presence of much cobalt can be performed by converting that metal into the form of cobalticyanide, which is not affected by the subsequent addition of formaldehyde to reconvert the nickel into the ionised condition.[40] Among the less common applications may be mentioned tests for bismuth,[41] copper,[42] cobalt,[43] and for the platinum metals, in particular palladium.[44]

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[27] *J.*, 1931, 105.

[28] F. Ephraim, *Ber.*, 1931, **64**, [*B*], 1215; *A.*, 1931, 813.

[29] W. Reif, *Mikrochem.*, 1931, **9**, 424; *A.*, 1931, 927; *Z. anal. Chem.*, 1932, **88**, 38; *A.*, 589.

[30] *J.*, 1931, 2003.

[31] F. Ephraim, *Ber.*, 1931, **64**, [*B*], 1210; *A.*, 1931, 813.

[32] *Ibid.*, p. 2819; *A.*, 160.

[33] *Ann. Chim. anal.*, 1925, **15**, 373; *A.*, 1926, 140.

[34] F. Feigl, *Ber.*, 1923, **56**, [*B*], 2083; *A.*, 1923, ii, 880.

[35] *Bur. Stand. J. Res.*, 1932, **9**, 1; *A.*, 1104.

[36] P. Slawik, *Chem.-Ztg.*, 1912, **36**, 54; *A.*, 1912, ii, 299; L. A. Tschugaev and B. P. Orelkin, *Z. anorg. Chem.*, 1914, **89**, 401; *A.*, 1915, ii, 489; W. Vaubel, *Z. öffentl. Chem.*, 1921, **27**, 163; *A.*, 1921, ii, 596; P. M. Koenig, *Chim. et Ind.*, 1922, **7**, 55; E. J. Kraus, *Z. anal. Chem.*, 1927, **71**, 189; *A.*, 1927, 746; R. Nakaseko, *Mem. Coll. Sci. Kyoto*, 1928, [*A*], **11**, 113; *A.*, 1928, 727.

[37] F. Ephraim, *Helv. Chim. Acta*, 1931, **14**, 1266; *A.*, 137.

[38] J. Dick, *Z. anal. Chem.*, 1929, **77**, 354; *A.*, 1929, 901.

8-*Hydroxyquinoline* (" oxine ") forms insoluble complex compounds with most metals, some of which were known for many years before their value in analytical operations was realised by R. Berg and F. L. Hahn independently about six years ago. Since that time the publication of well over fifty papers serves to indicate the interest which this reagent has aroused. The subject has been referred to in recent Reports, but it may be useful to make a recapitulation here.

In his first paper,[45] R. Berg presented in tabular form the reactions of the commoner metals in acetic acid, in ammoniacal, and in caustic alkaline solutions, and showed that in the last case, with tartrate also present, copper, magnesium, zinc, cadmium, and ferrous iron alone are precipitated—with the proviso that mercury, bismuth, manganese, cobalt, and nickel are partially precipitated when present in very large proportions. Of this " oxine " group of metals, the iron can be eliminated by prior oxidation and all except magnesium are precipitated from acetic solution.

The precipitates are crystalline, or can be made so by suitably warming the solutions, and can readily be filtered and washed. They can be weighed after drying at an appropriate temperature, usually 100°, or often after careful ignition to oxide, although this procedure involves the loss of the advantage of weighing a compound of high molecular weight; for example, the aluminium compound contains only 5·87% of the metal. Alternatively, a volumetric method may be applied whereby the oxine residue is titrated with standard bromate–bromide mixture; H. T. Bucherer and F. W. Meier[46] have applied their filtration method in the case of nickel and cobalt. For small quantities, a colorimetric process has also been described.[47]

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[39] A. A. Wassiljew and A. K. Sinkowskaja, *Z. anal. Chem.*, 1932, **89**, 262.

[40] F. Feigl and H. J. Kapulitzas, *ibid.*, 1930, **82**, 417; *A.*, 1931, 455.

[41] H. Kubina and J. Plichta, *ibid.*, 1927, **72**, 11; *A.*, 1927, 1048.

[42] S. G. Clarke and B. Jones, *Analyst*, 1929, **54**, 333; *A.*, 1929, 900.

[43] F. Feigl and L. von Tustanowska, *Ber.*, 1924, **57**, [*B*], 762; *A.*, 1924, ii, 504.

[44] M. Wunder and V. Thüringer, *Z. anal. Chem.*, 1913, **52**, 101, 660; *A.*, 1913, ii, 252, 884; A. Gutbier and C. Fellner, *ibid.*, 1915, **54**, 205; *A.*, 1915, ii, 493; A. M. Smoot, *Eng. and Min. J.*, 1915, **99**, 700; *B.*, 1915, 554; C. W. Davis, *U.S. Bur. Mines*, Rep. Investigations 2351 (1922); *A.*, 1922, ii, 662; H. E. Zschiegner, *J. Ind. Eng. Chem.*, 1925, **17**, 291; *A.*, 1925, ii, 443; R. A. Cooper, *J. Chem. Met. Min. S. Africa*, 1925, **25**, 296; *A.*, 1925, ii, 827.

[45] *J. pr. Chem.*, 1927, **115**, 178; *A.*, 1927, 674.

The most useful applications of this reagent are for magnesium[48] and aluminium.[49] For the determination of the former metal in particular it has already reached the technical text-books. The excess of reagent can readily be removed for subsequent determination of alkali metals, while separation from the alkaline-earth metals can also be effected, though double precipitation may be necessary. In the case of aluminium, the metal can be precipitated directly from solutions which contain organic compounds such as tartrates or glycerol which would have to be destroyed before the usual treatment with ammonia could be applied; other useful separations are from beryllium,[50] and from phosphate, borate, fluoride, uranium, titanium, etc.[51]

Many useful separations of metals can be effected by means of this reagent; in addition, it provides a useful means of bringing metals, which have been separated by other means, into a form suitable for weighing. Amongst the practical applications which have been described are the evaluation of some pharmacopœial salts and preparations,[52] the determination of the magnesium hardness of water,[53] of magnesium in Portland cement,[54] in blood[55] and in organic liquids,[56] the analysis of cadmium-red pigments involving separation of cadmium from selenate,[57] and its use in silicate analysis.[58]

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[46] *Z. anal. Chem.*, 1932, **89**, 161; *A.*, 1012.

[47] R. Berg, with W. Wolker and E. Skopp, *Mikrochem.*, Emich Festschr., 1930, 18; *A.*, 1930, 1546; W. A. Hough and J. B. Ficklen, *J. Amer. Chem. Soc.*, 1930, **52**, 4752; *A.*, 1931, 327.

[48] R. Berg, *Z. anal. Chem.*, 1927, **71**, 23; *A.*, 1927, 639; F. L. Hahn and K. Viewig, *ibid.*, p. 122; *A.*, 1927, 639; H. Fredholm, *Svensk Kem. Tidskr.*, 1932, **44**, 79; *A.*, 489.

[49] R. Berg, *Z. anal. Chem.*, 1927, **71**, 369; *A.*, 1927, 848; F. L. Hahn and K. Viewig, *loc. cit.* (ref. 48).

[50] I. M. Kolthoff and E. B. Sandell, *J. Amer. Chem. Soc.*, 1928, **50**, 1900; *A.*, 1928, 981; M. Niessner, *Z. anal. Chem.*, 1929, **76**, 135; *A.*, 1929, 285.

[51] G. E. F. Lundell and H. B. Knowles, *Bur. Stand. J. Res.*, 1929, **3**, 89; *A.*, 1929, 1260.

[52] H. Matthes and P. Schütz, *Pharm. Ztg.*, 1928, **73**, 353; *B.*, 1928, 501; I. M. Kolthoff, *ibid.*, 1927, **72**, 1173.

[53] K. V. Luck and H. J. Meyer, *Z. angew. Chem.*, 1928, **41**, 1281; *B.*, 1929, 114; M. E. Stas, *Pharm. Weekblad*, 1930, **67**, 1245; *B.*, 1931, 92.

[54] J. C. Redmond and H. A. Bright, *Bur. Stand. J. Res.*, 1931, **6**, 113; *B.*, 1931, 396.

[55] S. Yoshimatsu, *Mikrochem.*, 1931, **9**, 528; D. M. Greenberg and M. A. Mackay, *J. Biol. Chem.*, 1932, **96**, 416; *A.*, 764.

[56] C. Bomskov, *Z. physiol. Chem.*, 1931, **202**, 32; *A.*, 35.

Following the observation [59] that 5 : 7-dibromo-8-hydroxyquinoline gives a precipitate with copper salts even in mineral acid solution, the influence of various substituents on the solubility and stability of the complex metal compounds has been investigated.[60] Several of the 5 : 7-dihalogeno-derivatives form very insoluble compounds with copper, iron, and titanium, for which metals a scheme of separations has been described, based on the dibromo-derivative.[61]

Aliphatic diamines, *e.g.*, ethylenediamine, form certain insoluble complexes such as $(HgI_4)(Cu\ en_2)$, which has been applied to the determination of both mercury [62] and copper.[63] Cadmium forms an analogous compound,[64] but in the case of bismuth, the cobalt complex has the composition $(BiI_4)_2(Co\ en_3)I$ [65] (compare the compound $C_9H_7ON,HBiI_4$ given by bismuth with 8-hydroxyquinoline in the presence of iodide).[66] Propylenediamine can also be used in the mercury–copper complex.[67]

A compound of somewhat different character is $(Ni\ en_3)S_2O_3$, whose insoluble character permits the detection of thiosulphate in the presence of most sulphur oxy-acids, thiocyanate, and sodium sulphide; [68] this recalls the compound copper pyridine persulphate which serves to detect persulphate.[69]

Dialkyldithiocarbamates, which were proposed many years ago [70] for the detection of copper and iron, have been applied quantitatively to the determination of copper,[71] sodium diethyldithiocarbamate being the particular salt used. Since iron also gives a brown colour, it must be removed, and this has been effected by electrolytic deposition of the copper [72] or by means of citric acid; [73] the coloured copper salt can then be extracted by carbon tetrachloride. The method has been applied to ascertain the copper content of sea-water [74] and of certain pharmaceutical preparations and chemicals.[75] Piperidine pentamethylenedithiocarbamate, prepared commercially as an accelerator for vulcanisation, can be used for the same purpose.[76]

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[57] C. G. Daubney, *Analyst*, 1932, **57**, 22; *B.*, 234.

[58] J. Robitschek, *J. Amer. Ceram. Soc.*, 1928, **11**, 587; *B.*, 1928, 895; A. Benedetti-Pichler and F. Schneider, *Mikrochem.*, Emich Festschr., 1930, 1; *A.*, 1930, 1544; A. Granger, *Ceram. et Verrerie*, 1932, 137.

[59] R. Berg, *Z. anal. Chem.*, 1927, **70**, 341; *A.*, 1927, 436.

[60] *Idem*, *Z. anorg. Chem.*, 1932, **204**, 208; *A.*, 490.

[61] R. Berg and H. Kustenmacher, *ibid.*, p. 215; *A.*, 490; see also *idem*, *Mikrochem.*, Emich Festschr., 1930, 26; *A.*, 1930, 1546; V. Marsson and L. W. Haase, *Chem.-Ztg.*, 1928, **52**, 993; *A.*, 1929, 164; L. W. Haase, *Z. anal. Chem.*, 1929, **78**, 113; *A.*, 1929, 1159.

[62] G. Spacu and G. Suciu, *ibid.*, 1929, **77**, 334; **78**, 244; *A.*, 1929, 901, 1259.

[63] *Idem*, *ibid.*, p. 329; *A.*, 1929, 1413.

[64] *Idem*, *ibid.*, p. 340; *A.*, 1929, 900.

[65] *Idem*, *ibid.*, **79**, 196; *A.*, 1930, 184.

[66] R. Berg and O. Wurm, *Ber.*, 1927, **60**, [*B*], 1664; *A.*, 1927, 847.

[67] G. Spacu and P. Spacu, *Z. anal. Chem.*, 1932, **89**, 187; *A.*, 1011.

[68] *Idem*, *ibid.*, p. 192; *A.*, 1010.

[69] G. Spacu, *Bul. Soc. Stiinte Cluj*, 1923, **1**, 583.

[70] M. Delépine, *Bull. Soc. chim.*, 1908, [iv], **3**, 652; *A.*, 1908, ii, 633.

[71] T. Callan and J. A. R. Henderson, *Analyst*, 1929, **54**, 650; *A.*, 1930, 53.

Tetramethyldiaminodiphenylmethane (" tetramethyl-base ") has long been known as a reagent, qualitatively, for ozone [77] and for lead and manganese in their higher states of oxidation.[78] Although the blue coloration is not too stable, endeavours have been made to utilise the reaction quantitatively for lead [79] and for manganese; [80] permanent standards are prepared of mixtures of crystal-violet and methylene-blue. New ground is cut in reactions with vanadate and tungstate, the latter being applied quantitatively.[81]

Cupferron, which derived its name as a precipitant for copper and iron, is also known in the same capacity for titanium and zirconium; during the last ten years, further investigations have revealed other possibilities, in particular in the case of tin.[82] Conditions for the precipitation of mercurous mercury [83] and bismuth [84] are also described. It must not be overlooked that, in neutral solution, all metals except the alkalis are precipitated by cupferron and that such separations depend upon the varying solubilities of the salts in acid solutions.

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[72] F. Grendel, *Pharm. Weekblad*, 1930, **67**, 913, 1050, 1345; *B.*, 1930, 1089; W. R. G. Atkins, *J. Marine Biol. Assoc.*, 1932, **18**, 193; *A.*, 714.

[73] L. A. Haddock and N. Evers, *Analyst*, 1932, **57**, 495; *A.*, 1011.

[74] W. R. G. Atkins, *loc. cit.* (72).

[75] N. Evers and L. A. Haddock, *Quart. J. Pharm.*, 1932, **5**, 458.

[76] R. G. Harry, *Analyst*, 1931, **56**, 736; *A.*, 35.

[77] C. Arnold and C. Mentzel, *Ber.*, 1902, **35**, 1324; *A.*, 1902, ii, 352; F. Fischer and F. Brähmer, *Ber.*, 1906, **39**, 940; *A.*, 1906, ii, 224; F. Fischer and H. Marx, *ibid.*, p. 2555; *A.*, 1906, ii, 627.

[78] J. A. Trillat, *Compt. rend.*, 1903, **136**, 1205; *A.*, 1903, ii, 512; J. B. Ficklen, *Chem. and Ind.*, 1931, **50**, 869; *A.*, 1931, 1383.

[79] A. D. Petrov, *J. Russ. Phys. Chem. Soc.*, 1928, **60**, 311; *A.*, 1928, 726.

[80] R. G. Harry, *Chem. and Ind.*, 1931, **50**, 796; *A.*, 1931, 1385.

[81] M. Papafil and R. Cernatesco, *Ann. sci. Univ. Jassy*, 1931, **16**, 526; *A.*, 1931, 1386.

[82] A. Kling and A. Lassieur, *Compt. rend.*, 1920, **170**, 1112; *A.*, 1920, ii, 452; N. H. Furman, *J. Ind. Eng. Chem.*, 1923, **15**, 1071; *A.*, 1923, ii, 881; A. Pinkus and (Mlle.) J. Claessens, *Bull. Soc. chim. Belg.*, 1927, **36**, 413; *A.*, 1927, 848.

[83] A. Pinkus and (Mlle.) M. Katzenstein, *ibid.*, 1930, **39**, 179; *A.*, 1930, 1011.

[84] A. Pinkus and J. Dernies, *ibid.*, 1928, **37**, 267; *A.*, 1928, 1109.

α-Nitroso-β-naphthol is best known as a precipitant for cobalt,[85] although it has also been applied to the determination of palladium [86] and to the separation of iron from beryllium,[87] indium,[88] and gallium.[89] Since cupferron does not interfere with the subsequent precipitation of cobalt by nitrosonaphthol, the former reagent can be used to remove traces of iron left after ether extraction in the determination of cobalt in magnetic and high-speed tool steel.[90]

One of the drawbacks to the use of this reagent for cobalt is that the precipitate obtained is of indefinite composition and must therefore be subjected to further treatment to convert it into a form suitable for weighing. It has now been shown,[91] by first oxidising the cobalt and then working in an acetic acid solution of the cobaltic hydroxide obtained on addition of alkali, that a definite compound is obtained which can be dried at 130° without losing its two molecules of water. The process is particularly applicable to the analysis of cobaltic colours such as smalt.

An interesting test for cyanates,[92] applicable in the presence of most inorganic salts, consists in treating the dried silver salt, suspended in ether, with *cyclo*hexene and iodine; the pungent-smelling 2-iodo*cyclo*hexylcarbimide is formed. As cyanides also cause the formation of a somewhat similar-smelling compound, treatment of the test solution with ammonia to give a white, finely crystalline precipitate of the corresponding carbamide serves to diagnose cyanates.

The readiness with which sodium sulphite in solution becomes oxidised is not generally appreciated. Experiments at concentrations such as are used in volumetric work have shown [93] that such oxidation may amount to 30% in 30 minutes, but may be retarded for some hours by the addition of erythritol, glycol, or ethyl alcohol. In the case of sulphurous acid there is the additional danger of loss of sulphur dioxide although these errors may be reduced by the use in the analysis of a stronger oxidising agent than the usual iodine.[94] In general terms, acid sulphite solutions are more stable than neutral solutions.[95] These considerations also enter into determinations of sulphur dioxide in gases; thus M. D. Thomas and J. N. Abersold[96] found that substantial proportions of the dioxide absorbed in water from very dilute mixtures with air were oxidised. It follows that accurate determinations of the dioxide in gaseous mixtures can only be made if the scrubbing reagent can serve as the oxidising agent, *e.g.*, hydrogen peroxide or iodine–starch, or, if alkaline media are used, some stabilising substance such as has been mentioned above is also present; for this purpose H. F. Johnstone[97] found benzyl alcohol satisfactory.

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[85] M. Ilinski and G. v. Knorre, *Ber.*, 1885, **18**, 699; *A.*, 1885, 840.

[86] M. Wunder and V. Thüringer, *Z. anal. Chem.*, 1913, **52**, 737; *A.*, 1913, ii, 1080; W. Schmidt, *Z. anorg. Chem.*, 1913, **80**, 335; *A.*, 1913, ii, 440.

[87] M. Schleier, *Chem.-Ztg.*, 1892, **16**, 420; *B.*, 1892, 713; E. A. Atkinson and E. F. Smith, *J. Amer. Chem. Soc.*, 1895, **17**, 688; *A.*, 1896, ii, 220.

[88] F. C. Mathers, *ibid.*, 1908, **30**, 209; *A.*, 1908, ii, 434.

[89] J. Papish and L. E. Hoag, *ibid.*, 1928, **50**, 2118; *A.*, 1928, 981.

[90] See p. 221.

[91] C. Mayr and F. Feigl, *Z. anal. Chem.*, 1932, **90**, 15; *A.*, 1224.

[92] M. Linhard and M. Stephan, *Z. anal. Chem.*, 1932, **88**, 16; *A.*, 588.

[93] J. Lukas, *Chem. Listy*, 1932, **26**, 26; *A.*, 242.

The iodometric determination of persulphate has attracted much attention in recent years, and, although reports have, on the whole, been favourable,[98] yet erratic results have been recorded;[99] these have now been traced to the presence in the potassium iodide of a small quantity of organic impurity having a strong reducing action in alkaline solution.[1] Persulphates, including the ammonium salt, are decomposed by boiling for a short time with excess of pure neutral hydrogen peroxide, and the sulphuric acid formed can then be titrated with alkali.[2]

Organic Analysis.

Compounds having an enolic or allied structure have a reducing action on mercurous nitrate; the reaction is more general than that with ferric chloride but is also given by certain substances having active unsaturated groupings.[3]

During recent years, many derivatives have been described for the purposes of identification of numbers of various classes of compound. In the case of acids, particular attention has been paid to the phenacyl[4] and substituted phenacyl[5] esters. During the present year the lists have been extended in the case of the unsubstituted,[6] the *p*-halogeno-,[7] and *p*-phenyl-phenacyl[8] esters. In general, aliphatic acids when warmed with thionylaniline afford anilides.[9]

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[94] J. Bicskei, *Z. anorg. Chem.*, 1927, **160**, 64; *A.*, 1927, 330.

[95] H. M. Mason and G. Walsh, *Analyst*, 1928, **53**, 142; *A.*, 1928, 497.

[96] *Ind. Eng. Chem.* (*Anal.*), 1929, **1**, 14; *B.*, 1929, 282.

[97] *Univ. Illinois Bull.*, 1931, **28**, No. 41, 100.

[98] L. von Zombory, *Z. anal. Chem.*, 1928, **73**, 217; *A.*, 1928, 497; A. Schwicker, *ibid.*, **74**, 433; *A.*, 1928, 1107; C. V. King and E. Jette, *J. Amer. Chem. Soc.*, 1930, **52**, 608; *A.*, 1930, 441; J. H. van der Meulen, *Z. anal. Chem.*, 1932, **88**, 173; *A.*, 710.

[99] A. Kurtenacker and H. Kubina, *ibid.*, 1931, **83**, 14; *A.*, 1931, 451.

[1] A. Kurtenacker, *ibid.*, **88**, 171; *A.*, 710.

[2] J. H. van der Meulen, *Rec. trav. chim.*, 1932, **51**, 445; *A.*, 587.

[3] E. V. Zappi, *Bull. Soc. chim.*, 1932, [iv], **51**, 54; *A.*, 362.

2 : 4-Dinitrochlorobenzene readily reacts with alkyl and aryl sodium mercaptides to form sulphides which in turn may be converted into the corresponding sulphones by means of permanganate.[10] The *p*-toluenesulphonates of aromatic amines can, in general, be readily prepared in a pure state;[11] the *p*-nitrobenzyl derivatives of a number of amines have been described,[12] and the carbamates and carbamides derived from *p*-nitrophenylcarbimide with alcohols and amino-compounds.[13]

Pentabromoacetone, formed by the oxidation of citric acid by acid permanganate in the presence of bromide, reacts in alcoholic solution with sodium iodide; one molecule of citric acid in this way liberates six equivalents of iodine. This method is more rapid than those in which the bromo-compound is weighed.[14]

The claim by L. Nyns[15] for a copper–bicarbonate solution as specific for fructose has been disproved both in this country and in America. Maltose, dextrose, and arabinose reduce the reagent to a slight degree, the effect increasing in the order given. Nevertheless, the method is of value in sugar analysis, particularly when used in combination with other methods; by working at 55° instead of at 48·5—49°, the period of reduction may conveniently be reduced by one-half, *i.e.*, to 75 minutes.[16] Both phenolphthalein and alcohol react with iodine in the presence of alkali; in neutralising solutions prior to the oxidation of aldose sugars by alkaline iodine, the use of aqueous methyl-orange avoids the introduction of errors from this cause.[17]

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[4] J. B. Rather and E. E. Reid, *J. Amer. Chem. Soc.*, 1919, **41**, 75; *A.*, 1919, i, 157.

[5] W. L. Judefind and E. E. Reid, *ibid.*, 1920, **42**, 1043; *A.*, 1920, i, 480; R. M. Hann, E. E. Reid, and G. S. Jamieson, *ibid.*, 1930, **52**, 818; *A.*, 1930, 474; S. G. Powell, *ibid.*, 1931, **53**, 1172; *A.*, 1931, 621; N. L. Drake and J. Bronitsky, *ibid.*, 1930, **52**, 3715; *A.*, 1930, 1436.

[6] K. Chen, *Trans. Science Soc. China*, 1931, **7**, 73; *A.*, 529; W. Kimura, *J. Soc. Chem. Ind. Japan*, 1932, **35**, 221; *A.*, 946.

[7] K. Chen and C. Shih, *ibid.*, p. 81; *A.*, 529; C. G. Moses and E. E. Reid, *J. Amer. Chem. Soc.*, 1932, **54**, 2101; *A.*, 744; H. Lund and T. Langvad, *ibid.*, p. 4107; *A.*, 1249.

[8] N. L. Drake and J. P. Sweeney, *ibid.*, p. 2059; *A.*, 745.

[9] P. Carré and D. Libermann, *Compt. rend.*, 1932, **194**, 2218; *A.*, 867.

[10] R. W. Bost, J. O. Turner, and R. D. Norton, *J. Amer. Chem. Soc.*, 1932, **54**, 1985; *A.*, 719.

[11] C. R. Noller and P. Liang, *ibid.*, p. 670; *A.*, 375.

[12] E. Lyons, *J. Amer. Pharm. Assoc.*, 1932, **21**, 224; *A.*, 502.

[13] C. W. van Hoogstraten, *Rec. trav. chim.*, 1932, **51**, 414; *A.*, 597.

[14] P. A. Kometiani, *Z. anal. Chem.*, 1931, **86**, 359; *A.*, 43.

[15] *Sucr. Belge*, 1924, **44**, 210; *B.*, 1925, 21.

Conditions are described for the quantitative determination of various carbonyl compounds by formation of 2 : 4-dinitrophenylhydrazones; the method has been applied to camphor, menthone, pulegone, citral, furfuraldehyde, methylfurfuraldehyde, and santonin.[18]

B. A. Ellis.
J. J. Fox.

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[16] R. F. Jackson and J. A. Matthews, *Bur. Stand. J. Res.*, 1932, **8**, 403; *A.*, 835.

[17] (Miss) C. A. Mallen, *Analyst*, 1932, **57**, 244; *A.*, 603.

[18] O. Fernández, L. Sociás, and C. Torres, *Anal. Fis. Quim.*, 1932, **30**, 37; *A.*, 411; O. Fernández and L. Sociás, *ibid.*, p. 477; *A.*, 948; E. Simon, *Biochem. Z.*, 1932, **247**, 171; *A.*, 763.

BIOCHEMISTRY.

CONTINUED interest in the chemistry of the vitamins, and the considerable advances achieved during the past year, justify the attention which is again given to this field. Of outstanding interest, too, is the development of the recent work on the secondary sex hormones, more especially in relation to the striking advances in the chemistry of the cholane series. Of the other subjects dealt with this year in the section of animal biochemistry, particular attention is directed to the new and promising work on urea formation in the liver, and to the progress made in the investigation of carcinogenic hydrocarbons.

In the section of plant biochemistry the general arrangement of the last Report has been retained. Undiminished interest in the mineral nutrition of plants is again apparent, and the steady advancement in the elucidation of the varied metabolic processes of moulds is continued. A section dealing with certain plant enzymes and their activation is necessitated by the activity of workers in this field. The admirable work of R. and G. M. Robinson on the anthocyanin pigments marks a very great advance in this subject. The scope of the published work is too wide for adequate treatment here and reference to detail should be made in the original papers.

ANIMAL BIOCHEMISTRY.

Secondary Sex Hormones.

The last few years have witnessed a steadily increasing activity in the investigation of the internal secretory products responsible for the control of the development of the secondary sex characters of the male and the female animal. In particular, during the past year, considerable advances have been made in the elucidation of the structures of these interesting substances. These advances are mainly due to the new structural conception of the cholane series (bile acids and sterols) introduced by O. Rosenheim and H. King [1] and developed by them [2] and by the German workers, notably H. Wieland and E. Dane.[3] At the time of writing it seems clear that two substances, or types of substance, have been reasonably well characterised. The first of these is the follicular hormone which in animals produces oestrous, and influences the growth and course of development of the secondary female sex characters. It is also claimed that this substance accelerates the formation of flower and fruit buds in plants,[4] and it has been stated that the hormone, or substances closely resembling it in structure and properties, may be obtained from plant sources. Thus, a crystalline substance of this type has been isolated from palm-kernel extracts.[5] The second sex hormone is the testicular hormone isolated in a crystalline condition from male urine. It would appear to be closely related structurally to the follicular hormone and it is suggested that both have the same basal constitution as that of the members of the cholane series, namely, a tetra-nuclear structure comprised of a three-ring phenanthrene system with an additional five-membered ring.

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[1] *J. Soc. Chem. Ind.*, 1932, **51**, 464.

[2] *Ibid.*, p. 954.

[3] *Z. physiol. Chem.*, 1932, **212**, 41, 263.

The Follicular Hormone.—In the Reports for the last two years [6] the isolation and initial steps in the investigation of this hormone have been recorded. It has now become possible, in view of the newer work on the cholane series, to suggest a structure for the hormone and for the related inactive alcohol, pregnandiol, isolated along with the hormone from the urine of pregnancy. A. Butenandt [7] suggests that many substances with a similar hormone activity and closely related to one another may exist, but on the basis of present work it is clear that the most important are the α-follicular hormone (ketohydroxyoestrin, $C_{18}H_{22}O_2$) and its hydrate (trihydroxyoestrin, $C_{18}H_{24}O_3$). The investigations of Marrian [8] and of Butenandt [9] and their respective colleagues have led to the following conclusions. The hydroxy-ketone is formed from the hydrate by loss of water from two neighbouring hydroxyl groups. The third hydroxyl is acidic. Catalytic hydrogenation yields a hexahydro-derivative in the form of a saturated hydrocarbon $C_{18}H_{30}$. Zinc distillation yields the aromatic hydrocarbon $C_{18}H_{14}$. The three double bonds inferred to be present are in the same ring and this also carries the acidic hydroxyl, whereas the alcoholic hydroxyls of the hydrate are in a saturated ring. It is therefore suggested that the hormone is a condensed system consisting of a benzene ring and three saturated rings. *X*-Ray crystallographic measurements by J. D. Bernal,[10] and an investigation of unimolecular surface films by N. K. Adam and his colleagues,[11] and by J. F. Danielli [12] show that the saturated ring carrying the ketonic group and the benzene ring carrying the acidic hydroxyl are at opposite ends of the molecule.

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[4] W. Schoeller and H. Goebel, *Biochem. Z.*, 1932, **251**, 223; *A.*, 1068 (see also *A.*, 1931, 1337).

[5] A. Butenandt, *Angew. Chem.*, 1932, **45**, 655.

[6] *Ann. Reports*, 1930, **27**, 271; 1931, **28**, 236.

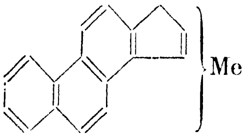
[7] *Loc. cit.* See also A. Butenandt and I. Störmer, *Z. physiol. Chem.*, 1932, **208**, 129; *A.*, 781.

[8] G. F. Marrian and G. A. D. Haslewood, *Biochem. J.*, 1932, **26**, 25; *A.*, 655.

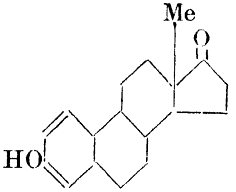
[9] *Loc. cit.* See also *Nature*, 1932, **130**, 238; *A.*, 971.

[10] *J. Soc. Chem. Ind.*, 1932, **51**, 259.

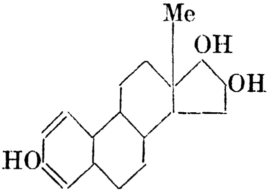
The facts outlined in the foregoing are expressed in the formulæ appended. (I) is the hydrocarbon $C_{18}H_{14}$, (II) is ketohydroxyoestrin, $C_{18}H_{22}O_2$, first obtained by Butenandt, and (III) is trihydroxyoestrin, $C_{18}H_{24}O_3$, first obtained by Marrian.



(I.)

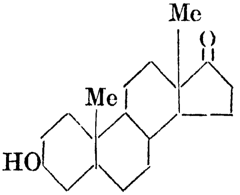


(II.)

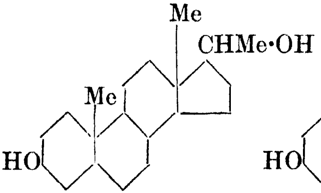


(III.)

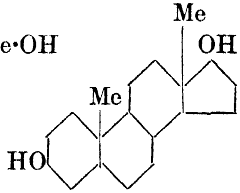
Testicular Hormone.—This hormone in a crystalline state has been obtained by A. Butenandt [13] (with K. Tscherning) from male urine. Its isolation from testes is also claimed in an earlier communication by B. Frattini and M. Maino,[14] whose preparation was less well characterised and probably much less pure than that of Butenandt.[15] The testicular substance is closely related to the follicular hormone and is also a hydroxy-ketone. It is saturated and possesses no acidic properties. Its melting point is given as 178° and its composition is $C_{18}H_{28}O_2$ or $C_{19}H_{30}O_3$, although its homogeneity is still in doubt. Butenandt [16] has tentatively suggested the formula (IV). Its activity would seem to be of a high order, since a total quantity of 1 to 1·2 γ administered in four doses over a period of two days produced a 30—35% increase in comb growth in cocks.



(IV.)



(V.) Pregnandiol



(VI.) $C_{19}H_{32}O_2$ Alcohol

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[11] N. K. Adam, J. F. Danielli, G. A. D. Haslewood, and G. F. Marrian, *Biochem. J.*, 1932, **26**, 1233; *A.*, 1173.

[12] *J. Soc. Chem. Ind.*, 1932, **51**, 1075.

[13] *Loc. cit.* See also *Z. angew. Chem.*, 1931, **44**, 905; *A.*, 96.

[14] *Arch. Ist. biochim. ital.*, 1930, **2**, 639; *A.*, 1931, 398. See also *Biochem. Z.*, 1932, **253**, 202; *A.*, 1173.

[15] *Angew. Chem.*, 1932, **45**, 324; *A.*, 781.

[16] *Loc. cit.*

The Origin of the Sex Hormones.—The present state of the investigations just outlined leads to the conclusion that the sex hormones are oxidation products of the bile acids and sterols, the process involving the breakdown of side chains and the conversion of a saturated into an aromatic ring with associated loss of a methyl group (compare the conversion of ergosterol, $C_{28}H_{44}O$, into neoergosterol, $C_{27}H_{40}O$).[17] This view of the relationship of the sex hormones to the cholane series gains in probability from the isolation of pregnandiol, $C_{21}H_{36}O_2$, together with two other inactive products, an alcohol, $C_{19}H_{32}O_2$ (m. p. 232°), and a hydroxy-ketone (m. p. 176·5°) isomeric with the testicular hormone. These substances, for which the formulæ (V) and (VI) are suggested, may readily be fitted into the general scheme as intermediate steps in the biological formation of the active products.

G. F. Marrian and G. A. D. Haslewood [18] have recorded the isolation from pregnant mare's urine of a dihydroxyphenol, $C_{15}H_{12}O(OH)_2$, m. p. 189—190·5°, to which they have given the name equol. It is physiologically inactive. If this compound is related to those already discussed, it would seem to be a derivative in which the three-ring phenanthrene nucleus alone persists with one additional carbon, but at the time of writing evidence of the relationship of equol to previously described compounds is lacking.

Isomeric Follicular Hormones.—Reference has already been made to the possible existence of closely related substances with similar hormone activities. A. Butenandt and I. Störmer [19] state that, when water is eliminated from trihydroxyoestrin by distillation over potassium hydrogen sulphate, there are formed α- and β-hydroxy-ketones which form mixed crystals and are both physiologically active. The α-isomeride is the original hormone of Butenandt, and the existence of the two forms is ascribed to a *cis-trans* isomerism. E. Schwenk and F. Hildebrandt [20] have isolated from mare's urine a further isomeride for which they claim a physiological activity higher than that of the α-hormone of Butenandt. A. Girard and his collaborators [21] have also described isomeric crystalline preparations isolated, in addition to the α-hormone, from mare's urine. These appear to have an oestrogenic activity about one-eighth that of the α-follicular hormone. Whether these substances are pure isomeric hormones of lower physiological activity, or mixed crystals of active and inactive components, remains an open question, but there seems to be little doubt concerning the existence of isomerides in this interesting group of substances.

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[17] H. H. Inhoffen, *Annalen*, 1932, **497**, 130.

[18] *Biochem. J.*, 1932, **26**, 1227; *A.*, 1156.

[19] *Loc. cit.*

[20] *Naturwiss.*, 1932, **20**, 658; *A.*, 1173.

[21] A. Girard, G. Sandulesco, A. Fridenson, and I. J. J. Rutgers, *Compt. rend.*, 1932, **194**, 909, 1020; *A.*, 433, 547.

A Substance Present in the Testicle which Increases Tissue Permeability.

F. Duran-Reynals in 1928[22] and 1929[23] described a testicular extract which much increased the lesions produced by intradermal inoculation of vaccine virus. D. McClean[24] made further observations on this interesting substance, and showed that it increased the permeability of the dermis so much that the bleb following the injection immediately disappeared and the inoculum diffused through an increased area of the dermis. Extracts of spermatozoa were shown to possess the same activity as extracts of the whole testicle. This suggested that the phenomenon is connected with the germinal activity of the testicle and is not a fortuitous property of the interstitial tissue of the gland. A possible association of the active substance with the sudden change in the permeability of the ova on fertilisation was suggested. W. T. J. Morgan and D. McClean[25] have now described the purification of the active testicular extracts, and the preparation of a highly active dry material. The latter has $[\alpha]_D - 10°$, nitrogen 10%, and amino-nitrogen 1·5%. The Molisch test is negative and all protein tests are positive. The active substance is not adsorbed from aqueous solution by benzoic acid. The minimal dose producing definite diffusion in the skin of the rabbit is 0·00001 milligram.

Secretin.

During the past year two papers dealing with the preparation and chemical properties of secretin have appeared. In 1928, J. Mellanby[26] described a method for preparing the hormone secretin which gave a product free from the depressor substance always present in acid extracts of the duodenal mucosa. He now describes an improved and simpler method:[27] the product contains C, 49·1; H, 6·9; N, 13·8; S, 1·5; ash, 1·17; O (by difference), 28·5%, but no phosphorus. These figures, together with the physical properties of secretin, suggest to Mellanby that secretin is a polypeptide. It is rapidly destroyed by trypsin-kinase, but is not acted upon by enterokinase or by trypsin in freshly secreted pancreatic juice. The yield is about 10 milligrams from 500 grams of intestinal mucosa. Secretin does not dialyse from aqueous solution through a collodion membrane. Its physiological actions are: (1) the production of a large volume of pancreatic juice; (2) the contraction of intestinal muscle; (3) the secretion of a small quantity of bile.

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[22] *Compt. rend. Soc. Biol.*, 1928, **99**, 1908.

[23] *J. Exp. Med.*, 1929, **50**, 327.

[24] *J. Path. Bact.*, 1930, **33**, 1045; 1931, **34**, 459.

[25] *J. Soc. Chem. Ind.*, 1932, **51**, 912. [26] *A.*, 1928, 1403.

[27] *Proc. Roy. Soc.*, 1932, [*B*], **111**, 429; *A.*, 1171.

A paper by R. N. Cunningham [28] also describes the preparation of secretin free from depressor substances, insoluble proteins, and inorganic salts. Cunningham's conclusion is that secretin is a secondary proteose. It passes through cellophane, but is retained by collodion membranes permeable to peptones. The results of Mellanby and Cunningham are, therefore, substantially in agreement, especially in regard to the peptide structure of their respective materials. There is, however, some divergence of opinion regarding the molecular dimensions of secretin.

Urea Formation in the Animal.

An important paper by H. A. Krebs and K. Henseleit [29] dealing with the formation of urea in the animal body opens up new aspects which may well prove to be fundamental. The authors have studied the rate of synthesis of urea from carbon dioxide and ammonia in surviving tissue sections of rat's organs. The methods employed reveal the liver as the sole organ in which this synthesis occurs, and in this organ the rate of synthesis is greatly increased by the presence of ornithine. This amino-acid acts as a catalyst, since it is not used up and small amounts effect a large synthesis. Similar results are obtained with arginine in virtue of its conversion into ornithine in the liver. On the other hand no increased urea formation was observed in the presence of glycine, *dl*-alanine, *d*-valine, *l*-leucine, *d*-cysteine, asparagine, aspartic acid, glutamic acid, phenylalanine, tyrosine, putrescine, cadaverine, lysine, creatine, guanidine, choline, tryptophan, or histidine. Apart from ornithine and arginine, the only other amino-acid effective in producing increased urea synthesis is citrulline. This acid was isolated by Y. Koga and S. Odake [30] in 1914 from the water melon (*Citrullus vulgaris*). Its constitution was established by M. Wada [31] by synthesis. It is α-amino-δ-carbamidovaleric acid,

$$NH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H.$$

Its formation has been observed by D. Ackermann [32] when arginine is acted on by putrefactive bacteria in a suitable medium, and in general the formation of carbamido-acids from amino-acids is a well-established biological process.[33]

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[28] *Biochem. J.*, 1932, **26**, 1081; *A.*, 1171.

[29] *Z. physiol. Chem.*, 1932, **210**, 33; *A.*, 1059.

[30] *J. Tokyo Chem. Soc.*, 1914, **35**, 519.

[31] *Proc. Imp. Acad. Tokyo*, 1930, **6**, 15; *A.*, 1930, 1224. See also *Biochem. Z.*, 1930, **224**, 420.

[32] *Z. physiol. Chem.*, 1931, **203**, 66; *A.*, 196.

In accelerating urea formation citrulline is consumed in the process and furnishes one atom of nitrogen per molecule of urea. The respective actions of ornithine and citrulline in promoting urea synthesis in the liver are explained by Krebs and Henseleit as follows: (1) The formation of citrulline by the condensation of one molecule of ammonia and one of carbon dioxide with the δ-amino-group of ornithine; (2) the condensation of one molecule of citrulline with a second molecule of ammonia to form arginine; (3) the decomposition of arginine by arginase to form ornithine and urea.

$$\begin{array}{c}
NH_2\cdot[CH_2]_3\cdot CH(NH_2)\cdot CO_2H + NH_3 + CO_2 \\
\downarrow \\
NH_2\cdot CO\cdot NH\cdot[CH_2]_3\cdot CH(NH_2)\cdot CO_2H + H_2O \quad . \quad . \quad (1) \\
+ \downarrow NH_3 \\
NH_2\cdot C(:NH)\cdot NH\cdot[CH_2]_3\cdot CH(NH_2)\cdot CO_2H + H_2O \quad . \quad . \quad (2) \\
\downarrow \\
NH_2\cdot[CH_2]_3\cdot CH(NH_2)\cdot CO_2H + CO(NH_2)_2 \quad (3)
\end{array}$$

Optimal formation of urea in the liver sections is observed in the presence of 10 mg. per cent. of *d*-ornithine and 200 mg. per cent. of *dl*-lactate. Urea is not formed in liver pulps in which the cell structure is destroyed, and although its synthesis does not involve an increased oxygen consumption by the liver, the process is closely dependent upon respiration. It is of interest to note, in view of the currently accepted structural relationship of urea to ammonium cyanate, that the latter does not increase the urea formation in the liver. The next step in this interesting series of investigations would appear to be the attempted isolation of citrulline, or a suitable derivative, from a liver preparation actively forming urea. D. Ackermann[34] has failed to observe the fission of arginine into citrulline and ammonia on subcutaneous injection of arginine into a dog. Nor was this process observed in ox liver, kidney, muscle, spleen, goose liver, or liver and muscle of the crayfish. It will, however, be borne in mind that this conversion is the reverse of that postulated by Krebs and Henseleit.

These new observations are obviously of the greatest importance, but it must not be forgotten that the animal does not form urea from ammonia but from amino-acids, and it has not been possible, so far, to correlate the deaminisation process with ammonia production.

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[33] H. D. Dakin, *J. Biol. Chem.*, 1909, **6**, 240.

[34] *Z. physiol. Chem.*, 1932, **209**, 12; *A.*, 962.

Dyes and Urease.

In the Report of last year reference was made to the suggestive work of J. H. Quastel[35] on the toxic action of dyes and related compounds on various enzymes. These investigations have now been extended to urease.[36] In general it is found that acidic dyes are entirely inert and that most basic dyes are toxic. The toxicity of such dyes as brilliant-green is enhanced by substances, apparently of the nature of the unsaturated glycerides, present in soyabean oil, which act as highly specific mordants between urease and the basic triphenylmethane dyes. Urease may be protected from the toxic action of the various dyes by urea, α-amino-acids, sarcosine, ethylenediamine, methylamine, dimethylamine, hydrazine, and hydroxylamine. No protection is afforded by trimethylamine, betaine, urethane, methylurea, diethylurea, and oxamic acid. Of particular interest is the observation that potassium cyanate protects urease from the toxic action of brilliant-green, whereas ammonium carbamate has little or no effect. The underlying theory being that protection indicates a combination between the enzyme and the protective substance, this observation is evidence for the contention that cyanic acid, rather than carbamic acid, is produced from urea by urease. It should, however, be noted that sodium cyanate is entirely without protective action against toxic dyes.

Carcinogenesis by Pure Hydrocarbons.

The varied physiological activity of the cholane series and related polycyclic compounds lends added interest to an already interesting problem, the production of cancerous new growths by application to the skin of pure polycyclic hydrocarbons. That hydrocarbons can produce cancer in mice followed from the work of E. L. Kennaway,[37] who investigated the carcinogenic mixtures, which could consist only of hydrocarbons, produced by heating acetylene or isoprene in an atmosphere of hydrogen. The strong fluorescence of these and of other carcinogenic mixtures well recognised in medical practice (*e.g.*, gasworks tar, shale oil, heated petroleum, and products of the action of heat on various substances of biological origin such as cholesterol, yeast, skin, muscle, and hair) suggested that such hydrocarbons were of the polycyclic aromatic type. J. W. Cook, I. Hieger, E. L. Kennaway, and W. V. Mayneord[38] have prepared and examined the following compounds, composed entirely of condensed benzene rings, with the view of ascertaining their carcinogenic action if any : (1) all the six possible 4-ring compounds; (2) all the ten known compounds out of the fifteen possible 5-ring compounds; (3) some compounds containing six and eight rings, and others. The work has been extended by J. W. Cook.[39] Of these compounds it is found that 1 : 2 : 5 : 6-dibenzanthracene (I)[40] alone shows carcinogenic power. It retains this undiminished even when very highly purified; thus, it has been shown to be active in nine different media, and has produced cancer when applied to the skin of mice in a concentration of 0·003% in benzene. Less active are its 2′-methyl, 3′-methyl, 9-amino-, 9-methoxy, and 9 : 10-dibenzyl derivatives, and phenanthra-acenaphthene (II). The production of mesoblastic tumours in rats and mice following the intraperitoneal injection of 1 : 2 : 5 : 6-dibenzanthracene in a fatty medium has been described by H. Burrows.[41] The hydrocarbon was dissolved in lard in a concentration of 0·1%, and the tumours conformed to the usually accepted criteria of malignancy.

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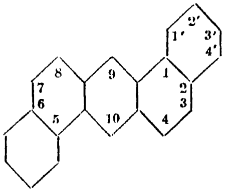
[35] *Ann. Reports*, 1931, **28**, 226.

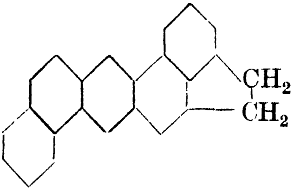
[36] J. H. Quastel, *Biochem. J.*, 1932, **26**, 1685.

[37] *J. Path. Bact.*, 1924, **27**, 234; *Brit. Med. J.*, 1925, **2**, 1; *Biochem. J.*, 1930, **24**, 497; *A.*, 1930, 807.

[38] *Proc. Roy. Soc.*, 1932, [*B*], **111**, 455; *A.*, 1156.

(I.)

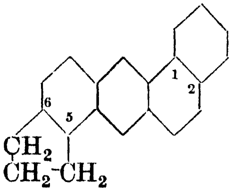


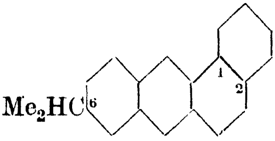


(II.)

More active even than 1 : 2 : 5 : 6-dibenzanthracene is 5 : 6-*cyclo*-penteno-1 : 2-benzanthracene (III), and the carcinogenic activity of 6-*iso*propyl-1 : 2-benzanthracene (IV) has also been established.

(III.)





(IV.)

Metastases in the axillary glands and lungs were obtained in five mice to which the *cyclo*penteno-compound was applied. The evidence so far obtained suggests that a molecular structure consisting of ring substituents attached to the 1 : 2- and 5 : 6-positions of the anthracene ring system is particularly efficacious in promoting carcinogenic activity. 1 : 2-Benzanthracene is itself inactive, and the inactivity of 2′ : 3′-phenanthra-1 : 2-anthracene

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[39] *Proc. Roy. Soc.*, 1932, [*B*], **111**, 485; *A.*, 1156.

[40] *Ann. Reports*, 1931, **28**, 126.

[41] *Proc. Roy. Soc.*, 1932, [*B*], **111**, 238.

(a six-ring compound) and of 4 : 5-benz-10 : 11-(1′ : 2′-naphtha)-chrysene (a seven-ring compound) indicates that the molecular complexity must be restricted within fairly narrow limits for the manifestation of carcinogenic activity.

Vitamin A.

Up to the present no crystalline preparation of vitamin A, or of a derivative of the vitamin, has been prepared, so that it is still not possible to state with certainty that the vitamin has been obtained in a state of purity. The characteristics of highly active preparations have been examined by I. M. Heilbron, R. N. Heslop, R. A. Morton, E. T. Webster, J. L. Rea, and J. C. Drummond,[42] and, after a comprehensive review of the position, it is concluded that the most potent preparations obtained by them and by Karrer and his colleagues,[43] both from mammalian and from fish-liver oils, are qualitatively and quantitatively indistinguishable in respect of ultra-violet absorption. If the products are not homogeneous, then either the non-vitamin material is relatively diactinic, or the preparations contain substances so closely alike that both exhibit the 328 mμ band. It is pointed out that it would indeed be curious if exactly the same proportion of material exhibiting negligible absorption were present in the products derived from various species of animals. But, on the other hand, the discovery that the isomeric α- and β-carotenes may both be transformed *in vivo* into vitamin A-like substances[44] points to the need for demonstrating, rather than assuming, strict homogeneity. Heilbron and his colleagues find their own observations are at least as consistent with the formula of Karrer[45] as with any alternative, and regard the weight of evidence as impressively, though not conclusively, in its favour. It is true that the experimental data on molecular weights[46] lead to a value of 320 ± 15 as against 286 on the basis of the Karrer formula. This is a small discrepancy, but doubts concerning purity are strengthened when the results of a very large number of ultimate analyses uniformly indicate values not quite consistent with the $C_{20}H_{30}O$ formula. The analysis of hydrogenation products from both crude and distilled vitamin A concentrates points to the presence of some contaminant in even the purest preparations. The question is not, however, one of gross impurity, and it is suggested that there may be present a small quantity of an alcohol more saturated than vitamin A.

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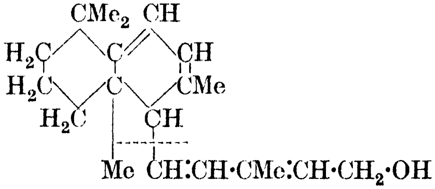
[42] *Biochem. J.*, 1932, **26**, 1178; *A.*, 1174.

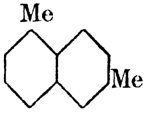
[43] P. Karrer, R. Morf, and K. Schöpp, *Ann. Reports*, 1931, **28**, 221; *Helv. Chim. Acta*, 1931, **14**, 1431; *A.*, 200.

[44] *Ann. Reports*, 1931, **28**, 219, 222. [45] *Ibid.*, p. 221. [46] *Ibid.*, p. 221.

A further communication from Heilbron, Morton, and Webster[47] records the extraordinary ease with which vitamin A (concentrate) is transformed into a cyclic derivative in the presence of hydrochloric acid and alcohol. Dehydrogenation of this product with selenium yielded 1 : 6-dimethylnaphthalene. On the basis of the Karrer formula (*q.v.*) these changes may be formulated as follows :



Cyclic product formed from vitamin A.



1 : 6-Dimethylnaphthalene.

Similar substituted naphthalenes are obtained from many bicyclic sesquiterpenes by dehydrogenation with sulphur or selenium. Thus the terpenoid nature of vitamin A is established, and there seems to be present in the richest concentrates a material which possesses as far as the 14th carbon atom the constitution advanced by Karrer, Morf, and Schöpp.[48]

Reference was made in the Report of last year to the claim of H. S. Olcott and D. C. McCann[49] regarding the conversion of carotene into vitamin A on incubating the hydrocarbon with fresh liver tissue *in vitro*. Further negative results have been recorded by J. L. Rea and J. C. Drummond,[50] and a critical survey, by B. Woolf and T. Moore,[51] of the technique upon which the claim was based leaves little doubt that further proof of the transformation is desirable.

An interesting observation regarding the action of antimony trichloride on carotene has been made by A. E. Gillam, I. M. Heilbron, R. A. Morton, and J. C. Drummond.[52] These workers find that on pouring into water the stable blue solution (λ max. 583—590 mμ) obtained by the interaction of the trichloride and carotene, the organic matter may be recovered free from antimony. The properties of the substance recovered agree with those of *iso*carotene, which is devoid of growth-promoting activity and is derived exclusively from the optically inactive β-carotene.[53] A study of the absorption spectra of the products of the action of antimony trichloride on carotene has led J. R. Edisbury, A. E. Gillam, I. M.

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[47] *Biochem. J.*, 1932, **26**, 1194; *A.*, 1174. [48] *Loc. cit.*

[49] *Ann. Reports*, 1931, **28**, 222; *A.*, 97.

[50] *Z. Vitaminforsch.*, 1932, **1**, 177; *A.*, 973.

[51] *Lancet*, 1932, **223**, 13; *A.*, 1174.

[52] *Biochem. J.*, 1932, **26**, 1174; *A.*, 1174.

[53] R. Kuhn and E. Lederer, *Ber.*, 1932, **65**, [*B*], 637; *A.*, 782.

Heilbron, and R. A. Morton [54] to suggest the partial conversion of the vitamin into hydronaphthalene derivatives.

Vitamin B_1.

The identity of the substance, or substances, comprising the crystalline preparations of vitamin B_1 still remains in doubt. S. Otake [55] has claimed that his anti-neuritic preparation (oryzanin) from rice bran yields an active hydrochloride, $C_6H_8O_2N_2,HCl$, m. p. 250°, resembling Jansen's crystalline vitamin B_1. A. Windaus and his collaborators [56] have obtained from yeast a highly active crystalline anti-neuritic preparation in which they revealed the presence of sulphur. On the basis of analyses of the crystalline picrolonate, they tentatively suggested the formula $C_{12}H_{17}ON_3S$ for the vitamin. The earlier work of A. G. van Veen [57] led him to suggest a formula very similar to that of Otake, namely, $C_6H_{10}O_2N_2,HCl$, but further investigation [58] has confirmed the presence of sulphur, and van Veen now suggests as the most probable formula for the hydrochloride, $C_{12}H_{20}O_2N_4S,2HCl$. The preparation agrees in melting point, chemical properties, and anti-neuritic activity with that of Windaus and his colleagues. The present position has been reviewed by R. Tschesche,[59] who concludes that the crystalline hydrochloride obtained from the Windaus preparation is identical with that of Jansen and Donath, which likewise contains sulphur.

The question of the purity of these preparations must still remain open, however, to judge from an examination of the problem by H. W. Kinnersley, J. R. P. O'Brien, and R. A. Peters.[60] These workers find that the crystalline hydrochloride, obtained from yeast by the charcoal adsorption methods of Kinnersley and Peters,[61] contains sulphur which cannot have been introduced during the isolation procedure. The crystalline hydrochloride has been prepared with an activity of 2—4 γ per diem (pigeon dose). A similar method of test showed the Jansen and Donath crystals from rice to have an activity of 5—8 γ per diem, and it was suggested that the preparation obtained by Peters and his colleagues was more potent than that of Windaus.[62] This has now been confirmed by direct test,[63] the vitamin B_1 units [64] per milligram being, for the Windaus preparation 260—280, and for the Peters preparation 470. The test used was the curative pigeon method. Moreover, Peters and his colleagues have found it possible to fractionate their crystalline preparation still further and they conclude that the Windaus preparation cannot be the pure vitamin B_1.

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[54] *Biochem. J.*, 1932, **26**, 1164; *A.*, 1174.

[55] *J. Agric. Chem. Soc. Japan*, 1931, **7**, 775; *A.*, 657.

[56] A. Windaus, R. Tschesche, H. Ruhkopf, F. Laquer, and F. Schultz, *Z. physiol. Chem.*, 1932, **204**, 123; *A.*, 310.

[57] *Rec. trav. chim.*, 1932, **51**, 265; *A.*, 433.

[58] A. G. van Veen, *Z. physiol. Chem.*, 1932, **208**, 125; *A.*, 782.

[59] *Chem.-Ztg.*, 1932, **56**, 166; *A.*, 547.

[60] *J. Physiol.*, 1932, **76**, 17P.

[61] "Chemistry at the Centenary Meeting of the British Association," Heffer and Son, Cambridge, 1932, p. 131.

[62] A. Windaus, *et al.*, *loc. cit.*

Vitamin C.

The year under review has seen a considerable extension of the chemical problems arising from the investigation of the anti-scorbutic vitamin. At the present time there seem to exist reasonable grounds for the belief that the vitamin has been isolated in a pure crystalline state.

First, reference must be made to a series of publications by Rygh and his collaborators. Results published early in 1932 by O. Rygh, A. Rygh, and P. Laland [65] made the interesting claim that ethereal extracts of neutralised orange-juice, possessing a high anti-scorbutic activity, yielded a syrup and crystalline narcotine. The latter is inactive against scurvy, but it was claimed that after irradiation with ultra-violet light it developed anti-scorbutic properties. It was suggested that this activity developed as a result of demethylation of the alkaloid, and it was further claimed that the *o*-diphenol resulting from this demethylation (methylnornarcotine), obtained by heating narcotine with concentrated hydrochloric acid for eight days at 100°, was highly active in protecting guinea-pigs from scurvy.[66] P. Laland [67] stated that narcotine was present in unripe tomatoes, cabbages, and potatoes, and the underlying theory seemed to involve the formation of active demethylated products during ripening. Further investigation of this interesting theory by R. L. Grant, S. Smith, and S. S. Zilva,[68] O. Dalmer and T. Moll,[69] W. A. Waugh and C. G. King,[70] J. Tillmans and P. Hirsch,[71] E. Ott and K. Packendorff,[72] and J. Brüggemann [73] has failed to corroborate the original claim. A recent paper by O. Rygh and A. Rygh [74] seems to imply a modification of the original claim in that it is now suggested that the active substance may be a combination of methylnornarcotine with a uronic acid.

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[63] H. W. Kinnersley, J. R. O'Brien, and R. A. Peters, *Nature*, 1932, **130**, 774.

[64] Medical Research Council, *Pharm. J.*, 1932, **129**, 5; *A.*, 886. (12 mg. Jansen acid clay = 1 pigeon dose.)

[65] *Z. physiol. Chem.*, 1932, **204**, 105, 114; *A.*, 310.

[66] See also O. Rygh, *Z. Vitaminforsch.*, 1932, **1**, 134; *A.*, 783; A. W. Owe, *Tidsskr. Kjemi Berg.*, 1931, **11**, 120; *A.*, 201.

[67] *Z. physiol. Chem.*, 1932, **204**, 112; *A.*, 311.

[68] *Biochem. J.*, 1932, **26**, 1628; *J. Soc. Chem. Ind.*, 1932, **51**, 166.

[69] *Z. physiol. Chem.*, 1932, **209**, 211; *A.*, 1069.

[70] *J. Biol. Chem.*, 1932, **97**, 325; *A.*, 973. [71] *Biochem. Z.*, 1932, **250**, 312.

[72] *Z. physiol. Chem.*, 1932, **210**, 94. [73] *Ibid.*, **211**, 231. [74] *Ibid.*, p. 275.

A much more general acceptance has been accorded to striking new results for which A. Szent-Györgyi [75] is responsible. In 1928 Szent-Györgyi,[76] in studying peroxidase systems, isolated from the cortex of the suprarenal glands a crystalline substance, $C_6H_8O_6$, isomeric with the lactone of glucuronic acid, and apparently belonging to the uronic acid group, which he referred to simply as hexuronic acid. The substance possessed strong reducing properties and was presumed to be, on very good evidence, the same substance as that responsible for the reducing power of many plant extracts. The pure compound has been studied by E. L. Hirst and R. J. W. Reynolds [77] and, on the basis of their results, W. N. Haworth [78] ascribed to it the constitution of a 6-carboxylic acid of a ketohexose. A crystalline monoacetone derivative has been described,[79] and further chemical investigations by E. G. Cox, E. L. Hirst, and R. J. W. Reynolds [80] have led them to suggest the following tautomeric structures :

$$CO_2H{\cdot}CO{\cdot}C(OH){:}CH{\cdot}CH(OH){\cdot}CH_2{\cdot}OH \rightleftarrows CO_2H{\cdot}CO{\cdot}CO{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$$

The double bond in the enolic modification readily accounts for the strong reducing properties, similar behaviour having been observed in an unsaturated trimethyl derivative of glucurone (the lactone of glucuronic acid), prepared synthetically by J. Pryde and R. T. Williams.[81] The hexuronic acid of Szent-Györgyi does not form a lactone, so that, although it is isomeric with the lactone of a typical hexuronic acid, strictly speaking it does not belong to this group of compounds. Szent-Györgyi and Haworth have suggested the name " ascorbic acid " in place of the previously used " hexuronic acid." [81a]

Hexuronic acid can be oxidised reversibly and irreversibly, and it is to the double function of oxidation and reduction in the reversible change that the acid probably owes its biological activity. The parallelism between the reducing power and the anti-scorbutic potency of plant extracts has been investigated in a series of well-documented researches by S. S. Zilva and his collaborators,[82] and more recently by J. Tillmans, P. Hirsch, and J. Jackisch.[83] The

[75] *Nature*, 1932, **129**, 943; *A.*, 886.

[76] *Biochem. J.*, 1928, **22**, 1387.

[77] *Nature*, 1932, **129**, 576; *A.*, 548.

[78] *Ibid.*, p. 576; *A.*, 548.

[79] L. v. Vargha, *ibid.*, **130**, 847.

[80] *Ibid.*, p. 888.

[81] *Ibid.*, 1933, **131**, 57.

[81a] *Ibid.*, p. 24.

[82] *Ann. Reports*, 1927, **24**, 247; 1928, **25**, 270.

[83] *Z. Unters. Lebensm.*, 1932, **63**, 241, 267, 276; *A.*, 658.

latter workers claim to have shown that the vitamin C content and the reducing capacity are, under many conditions, strictly parallel. Moreover the reducing substance studied by them may be oxidised, like hexuronic acid, in a reversible and an irreversible manner.

Biological feeding experiments by J. L. Svirbely and A. Szent-Györgyi [84] show that guinea-pigs have been completely protected from scurvy for a period of ninety days by the administration of 1 mg. daily of pure hexuronic acid. This claim has been confirmed by W. A. Waugh and C. G. King [85] (who place the dose at 0·5 mg. per day), by O. Dalmer and T. Moll,[86] by S. S. Zilva,[87] and by L. J. Harris and J. R. M. Innes.[88] The protective amount of the pure acid, 0·5 to 1·0 mg. per day, is approximately that of the reducing substance present in the protective dose of plant extracts (*e.g.*, 1 to 1·5 c.c. of lemon juice). Harris and Innes [89] find that 1 mg. of hexuronic acid has an activity slightly greater than that of 1 c.c. of orange juice, and state that the raw suprarenal cortex has a high anti-scorbutic activity approximately equal to its hexuronic acid content. Hirst and his associates [90] have examined the absorption spectrum of de-citrated lemon juice and have estimated that the hexuronic acid content corresponds with the recorded evaluation of the anti-scorbutic activity of the isolated acid.

This body of evidence seems to afford reasonably conclusive proof that Szent-Györgyi's hexuronic acid is vitamin C, but one must reserve a final judgment. In particular one would call attention to the fact that, the identity of hexuronic acid and the vitamin being assumed, the protective dose is of a considerably higher order than that of the other vitamins as far as these are known.

Vitamin D.

Full details of the properties of the crystalline preparation of vitamin D obtained by the German workers have been published by A. Windaus, O. Linsert, A. Lüttringhaus, and G. Weidlich.[91] There is general agreement that the product obtained by them is identical with the calciferol of F. A. Askew, R. B. Bourdillon, *et al.*, which was described in the Reports of last year.[92] The German workers have also obtained the pyrocalciferol, first described by the British workers, together with an additive compound of pyrocalciferol and an isomeric alcohol. The structure of vitamin D now remains to be elucidated and there is little doubt that with the help of the Rosenheim–King cholane formula, and the consequent advances in our knowledge of the chemistry of the sterols, this problem will soon be materially advanced.

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[84] *Biochem. J.*, 1932, **26**, 865; *A.*, 886. See also *Nature*, 1932, **129**, 576, 690; *A.*, 548, 657.

[85] *Loc. cit.*

[86] *Z. physiol. Chem.*, 1932, **211**, 284; *A.*, 1069.

[87] *Nature*, 1932, **129**, 943; *A.*, 887.

[88] *Lancet*, 1932, **223**, 235; *A.*, 1175.

[89] *Loc. cit.*

[90] E. G. Cox, E. L. Hirst, and R. J. W. Reynolds, *loc. cit.*

[91] *Annalen*, 1932, **492**, 226; *A.*, 311.

[92] *Ann. Reports*, 1931, **28**, 215.

With regard to the toxicity of large doses of vitamin D,[93] the view that this is an inherent property of the vitamin and is not due to a contaminant is supported by new results of Sir H. H. Dale, A. Marble, and H. P. Marks.[94] It is shown that pure calciferol has in dogs the same toxic action, in excessive doses, as the crude product obtained by irradiating ergosterol. The toxic action is obtained by intravenous injection as well as by oral administration, and the congestion of the alimentary mucosa, produced by such fatal doses, is equally pronounced with either method of administration. Of particular interest, in view of the association of the parathyroid gland with calcium metabolism, is the observation that complete parathyroidectomy does not prevent, or significantly hinder, the fatal intoxication produced by large doses of calciferol. At most it lowers the level of concentration reached by the blood calcium before death. The results, therefore, do not lend support to the view that vitamin D in excessive doses acts by promoting secretion of the parathyroid hormone, or by rendering the organism more responsive to its action.

PLANT BIOCHEMISTRY.

Mineral Nutrients and the Growth of the Higher Plants.

Mechanism of Nutrient Intake.—Considerable attention continues to be given to this important but complicated problem, more especially from the viewpoint of the mutual influence of ions on the rate of their absorption by the plant roots. Individual cases of inter-ionic effects are recorded in considerable number, but these have tended to emphasise a multiplicity of factors concerned rather than to yield data of a constructive nature. It would appear that more definite progress is likely to result from the careful application of the electro-physical concepts of the nature of electrolyte solutions and of membrane diffusion to the problems of plant nutrition. Thus, W. Thomas,[95] in a very suggestive discussion of the reciprocal action of nitrogen, phosphorus, and potassium in plant assimilation, illustrates the manner in which conflicting views of several aspects of ion absorption may be reconciled. The " selective " absorption of ions and the influence thereon of the hydrogen-ion concentration of the nutrient solution find explanation on the basis of the Donnan equilibrium and the physical factors controlling the mobility of ions. Diverse views of the physiological balance of nutrients in relation to Liebig's " Law of Minimum " and its corollary may be expressed as variants of the same basic phenomena. In a somewhat analogous attempt to link the nutrient absorption of plants with fundamental physico-chemical phenomena, H. P. Cooper[96] observes the close correlation between the proportions of elements in the ash of plants and their positions in the electromotive series. Since also there is a qualitative relationship between the order of removal of cations from soils by electrodialysis and their absorption by plants, it would seem that considerations of electrode- and ionisation-potentials of the elements concerned may afford a basis of explanation of the mechanism of the nutrient intake of plants. The effect of homologous series of ions on the growth of seedlings has been examined by K. Pirschle,[97] who shows that growth response is related to the position of the ion in the series and to the structure of the corresponding atoms. The current tendency to ascribe the control of the absorption of minerals to more purely physical forces and to minimise the effects of inherent physiological activity or adaptability of the plant is shown in a variety of papers. Thus J. Mucco[98] indicates the potential difference between plant leaves and the soil adjacent to the roots to be a controlling factor in the ratio of absorption of nutrient ions. Pirschle (*loc. cit.*) and F. C. Steward[99] show that temperature and light intensity, while affecting physiological activity in general, do not alter, to any marked extent, the relative order of intake of ions by plant cells. Both writers, too, emphasise the part played by carbon dioxide in maintaining a suitable hydrogen-ion concentration in the nutrient medium, thus compensating for the unequal penetration of anions and cations.

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[93] *Ann. Reports*, 1931, **28**, 218.

[94] *Proc. Roy. Soc.*, 1932, [*B*], **111**, 522; *A.*, 1176.

[95] *Soil Sci.*, 1932, **33**, 1; *B.*, 276.

Nitrogen Assimilation and Growth.—Differences in the response of plants to ammonium salts and to nitrates again form the basis of much experimental work. Although under conditions prevailing in normal soils the problem seldom arises, it becomes of considerable interest in the physiological aspect of internal nitrogen economy and metabolism. In many plants examined, the growth response to ammonium salts is optimal from nutrients having a neutral or slightly alkaline reaction, whereas nitrates are the more effective in acid-to-neutral media.[1, 2, 3] It is pointed out by V. Tiedgens and W. A. Robbins [2] that while ammoniacal nitrogen is absorbed by tomatoes over wide ranges of p_H, effective utilisation and elaboration into more complex bodies does not occur unless the media have $p_H > 7{\cdot}0$. It is possible that the accumulation of ammonia within the plant may become toxic in cases where the physiological detoxicating capacity of the plant (W. Ruhland and K. Wetzel [4]) is exceeded. The injurious effect is attributed by A. B. Beaumont and his colleagues [5] to a disturbance of normal metabolic processes. This view receives some support from observations of the altered intake of other nutrients occurring when nitrogen is supplied as an ammonium salt. Thus J. H. Purdo [6] ascribes the failure of sugar-cane plants grown with ammonium sulphate to a deficiency of adsorbed calcium. In experiments with cotton K. T. Holley, T. A. Pickett, and T. G. Dulin [7] show that the use of ammoniacal nitrogen in culture solutions leads to a much reduced intake of bases, especially calcium and magnesium.

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[96] *Soil Sci.*, 1930, **30**, 421; *B.*, 1931, 175; also *Proc. 2nd. Internat. Cong. Soil Sci.*, 1932, **4**, 164.

[97] *Jahrb. wiss. Bot.*, 1930, **72**, 335; 1932, **76**, 1; *A.*, 1931, 774; *B.*, 695.

[98] *Z. Pflanz. Düng.*, 1932, **24A**, 334; *A.*, 783.

[99] *Protoplasma*, 1932, **15**, 29; *A.*, 664.

Differences in growth response and composition of plants supplied with ammonium salts or with nitrate are recorded by R. M. Addoms and F. C. Mounce [8] in the case of cranberries. Ammonium salts produced much greater runner growth than did nitrates, low concentrations of which stimulated, and higher concentrations restricted, vegetative growth. Where urea was supplied to sugar-cane plants there was a characteristic increase in the number of suckers produced (Purdo, *loc. cit.*).

That nitrogen may be assimilated from more complex substances is shown by Beaumont (*loc. cit.*) in the case of tobacco, which can utilise urea, asparagine, and cystine but not arginine, alanine, glycine, leucine, acetamide, or cyanamide. A. I. Virtanen [9] records that aspartic acid is utilisable by legumes but not by cereals.

Potassium and the Growth and Composition of Plants.—The association of potassium in plants with respiratory activity and carbohydrate synthesis is of long standing, but in many instances attempts to elucidate definite numerical relationships have led to contradictory results. The gradual acceptance of the idea of "luxury consumption," *i.e.*, the intake of nutrients in amounts in excess of

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[1] *Ann. Reports*, 1931, **28**, 241.

[2] *New Jersey Agric. Exp. Sta. Bull.*, 1931, No. 536; *B.*, 1932, 567.

[3] R. M. Addoms and F. C. Mounce, *Plant Physiol.*, 1932, **7**, 643.

[4] *Ann. Reports*, 1930, **27**, 245.

[5] *J. Agric. Res.*, 1931, **43**, 559; *A.*, 1932, 101.

[6] *4th Cong. Internat. Soc. Sugar Cane Tech.*, 1932, Bull. 13; *B.*, 1932, 1047.

[7] *Georgia Agric. Exp. Sta. Bull.*, 1931, No. 169.

[8] *Plant Physiol.*, 1931, **6**, 653; *B.*, 1932, 201.

[9] *Suomen Kem.*, 1932, **5**, 67; *A.*, 975.

physiological requirement, has brought to light one source of misunderstanding in the potassium–carbohydrate relationships. This phenomenon, effectively demonstrated by F. Sekera [10] in 1928 and by other investigators since that time, would appear to be particularly marked in the case of potassium. Thus A. E. V. Richardson, H. C. Trumble, and R. E. Shapter [11] observe that during the migration of mineral substances from the leaves of grasses during maturation, nitrogen and phosphorus accumulate in stem bases and roots, but about one quarter of the total potash intake actually returns to the soil. This is possibly related to the fact that a very large proportion of the total potash content of plants remains in a soluble condition (G. Janssen and R. P. Bartholomew [12]) and as a result of rapid translocation, full physiological activity may be maintained by a minimum proportion of potassium. F. J. Richards [13] adds further evidence of the solubility of plant potash by indicating the probable leaching by rain of potash from leaves rich in that element but not from those of potash-deficient plants.

The function of potassium within the plant is not limited to its effect on carbohydrate metabolism. Relationships between potassium and nitrogen metabolism are indicated not only by the growth response of plants to suitably balanced nutrients, but also by examination of the nitrogen distribution of plants with regulated potash supply. This aspect of potash nutrition is discussed by Janssen and Bartholomew (*loc. cit.*), Richards (*loc. cit.*), and by G. Gassner and G. Goeze.[14]

The action of potassium in increasing the stiffness of cereal straws is examined by W. Acker,[15] who shows by physical measurements that the stability of barley straws increases with the potash supply to a maximum value corresponding to a definite N : P : K ratio. This maximum differs from that associated with the maximum crop yield. That definite modifications in the structure of the mechanical tissues (especially of the nodes) can be ascribed to variations in potash nutrition is shown by C. Blattny and V. Vukolov.[16]

Boron and Plant Growth.—Evidence of the necessity of this element for the growth of plants continues to be forthcoming.

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[10] *Z. Pflanz. Düng.*, 1928, **7B**, 533; *B.*, 1929, 67.

[11] *J. Counc. Sci. Ind. Res. Australia*, Bull. 66 (1932); *B.*, 1096.

[12] *J. Agric. Res.*, 1930, **40**, 243; *B.*, 1930, 387; also *J. Amer. Soc. Agron.*, 1932, **24**, 667.

[13] *Ann. Bot.*, 1932, **46**, 367; *A.*, 660.

[14] *Ber. deut. bot. Ges.* (*Festschr.*), 1932, **50A**, 412; *A.*, 890.

[15] *Pflanzenbau*, 1932, **9**, 104; *B.*, 1096.

[16] *Ernähr. Pflanze*, 1931, **27**, 355; *A.*, 1932, 204.

J. S. MacHargue and R. K. Calfee[17] show that in lettuce boron deficiency results in a type of leaf-burn and later in the death of tissues at the growing point. In plant metabolism boron cannot be replaced by any other element. Borax, but not boric acid, stimulates the growth of wheat[18] and of clover,[19] red clover appearing to be more sensitive than the grasses in this respect.

Boron injury to wheat occurs in nutrient solutions containing more than 5 p.p.m. of this element,[20] but F. M. Eaton[21] records that cotton plants do not produce maximum growth in nutrients containing less than the surprisingly high concentration of 10 p.p.m. Boron accumulation is most marked in leaves. Citrus leaves normally contain 100 p.p.m. of boron, but in trees injured by irrigation with water containing boron this value was increased to more than 1000 p.p.m.[22]

Calcium and Plant Growth.—The relatively few papers to be considered under this heading are concerned with the confirmation or elaboration of existing data rather than with the introduction of new subject matter. Calcium deficiency in tomatoes results in a chlorosis beginning in the upper stems and leaves, and, in addition to the characteristic decay of root tips, there is a sloughing of cells in the upper portions of the root. This is ascribed to the incomplete development of calcium pectate in the middle lamella. Deficient plants fail to assimilate nitrate and accumulate carbohydrates, although sugar translocation and starch digestion appear to be undisturbed. Granular proteinaceous inclusions also appear. The calcium in deficient plants is almost entirely insoluble and its rate of utilisation so small that normal cellular structure in the tissues cannot be maintained.[23] In an examination of calcium-deficient apple trees M. B. Davis[24] records increased shoot growth and production of enlarged leaves in the early stages of deficiency, followed by tissue breakdown later. The total ash content of such trees is abnormally low and contains a relatively high percentage of potassium and magnesium but low proportions of calcium and phosphorus. W. A. Albrecht and H. Jenny[25] show that calcium deficiency is an important factor in the appearance of " damping off" of soya bean seedlings, and at all ranges between p_H 3·8 and 6·9 an increased calcium supply in the nutrient reduces the number of diseased plants. In this respect calcium is a much more active agent than magnesium or potassium.

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[17] *Plant Physiol.*, 1932, **7**, 161; *B.*, 441.

[18] H. S. Morris, *Bull. Torrey Bot. Club*, 1931, **58**, 1; *A.*, 1932, 664.

[19] R. E. Guilbert and F. R. Pember, *Plant Physiol.*, 1931, **6**, 727; *B.*, 1932, 200.

[20] H. S. Morris, *loc. cit.*

[21] *Soil Sci.*, 1932, **34**, 301; *B.*, 1129.

[22] C. S. Scofield and L. V. Wilcox, *U.S. Dept. Agric. Tech. Bull.*, 1931, No. 264; *B.*, 1932, 317.

[23] G. T. Nightingale, *et al.*, *Plant Physiol.*, 1931, **6**, 605; *A.*, 1932, 205.

[24] *J. Pomology*, 1930, **8**, 316; *A.*, 1931, 273.

[25] *Bot. Gaz.*, 1931, **92**, 263; *B.*, 1932, 200.

Intake and Distribution of Mineral Substances during Growth.—Among a number of investigations on this subject reference should be made to the work of H. Wagner on oats [26] and sugar beet.[27] In oats the general decline in the percentage of nitrogen, phosphate, and potassium with growth is temporarily interrupted at the period of shoot production and again at the blossoming stage. The total content of the nutrients in the stems and leaves reaches a maximum prior to the period of active seed formation and is followed by a movement of nitrogen and phosphorus from stems and leaves and of potassium from leaves only, into the maturing seed. In general the maximum intake of nutrients by stems and leaves precedes that of organic matter production, but in flowers and seeds the two maxima are practically simultaneous. In the case of sugar beet the general decline in percentage nutrient contents of leaves with growth was limited largely to nitrogen until the period of rapid sugar accumulation; the percentage of potassium then decreased somewhat and that of calcium considerably. The percentage of phosphorus did not change appreciably throughout the first year of growth. The rates of nutrient intake and organic matter production in the first-year leaves were closely parallel, but in the second-year leaves mineral intake preceded the formation of organic matter. In this respect and also in the translocation of minerals from leaves to seeds the second-year growth of beet resembled that of oats. Along analogous lines the assimilation and translocation of minerals in the wheat plant are examined by F. Knowles and J. E. Watkin.[28] The total intake of nutrients by wheat plants increased steadily until after the emergence of the ears. The subsequent intake declined in rapidity and the individual elements attained their maximum values at varying periods prior to harvesting, *viz.*, potassium, 7 weeks; calcium, chlorine, 5 weeks; nitrogen, 3 weeks; carbon, phosphorus, silica, 2 weeks. The translocation of nutrients from stems to grain ceased one week before harvesting. Indications of a downward movement of potassium, calcium, and chlorine with approaching maturity are recorded. The nitrogen content of the organic matter of the ear decreased as maturity approached. An investigation of the soya bean by H. L. Borst and L. E. Thatcher [29] reveals a general similarity in the nutrient intake but with certain characteristic divergences. Thus the general decrease in the percentage of nutrients in the plants with advancing age is interrupted, in the case of nitrogen by a period of increase toward maturity. The mature seed contained more than one half of the plant's total nitrogen, a great proportion of potassium and a smaller proportion of calcium than any other organ of the plant.

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[26] *Z. Pflanz. Düng.*, 1932, **25A**, 48; *B.*, 696. [27] *Ibid.*, p. 129; *B.*, 811.

[28] *J. Agric. Sci.*, 1931, **21**, 612; *B.*, 1932, 38.

[29] *Ohio Agric. Exp. Sta. Bull.*, 1931, No. 494; *A.*, 1932, 436.

Plant Saps.—Continued interest in this subject is manifest during the period under review. Variations in composition resulting from diverse methods of extraction have been clarified to some extent by further work of J. D. Sayre and V. H. Morris.[30] In successive fractions of sap obtained from maize by increasing pressure the definitely soluble materials, total- and reducing-sugars, nitrate, and inorganic phosphate remain constant. Other constituents which may be presumed to occur, at least partially, in a colloidal condition, *e.g.*, total solids, total nitrogen, and phosphorus, tend to decrease as the pressure rises. It is concluded that in so far as the constituents in true solution are concerned the sap composition is representative of that of the whole plant. The reaction of saps has been examined by K. Böning and E. Böning-Seubert,[31] who show that in tobacco the nature of the nutrient does not markedly affect the p_H of leaf juices but does produce a considerable effect on the buffer capacity. Correlation between buffer index curves of the sap and the composition of the sap are indicated. Calcium-deficient plants show a rather high p_H and low buffer capacity in the sap, and vice versa. Deficiency of potassium and phosphate produces a highly buffered sap, and an excess of acidic ions in the nutrient a poorly buffered sap. Iron distribution in plants and the p_H of the sap appear to be closely related,[32] high p_H being associated with low soluble- and high total-iron contents, and low p_H with high soluble- and low total-iron contents. The sensitiveness of the condition of iron and presumably of its physiological functions in plants to changes in light intensity is revealed by the observation that diurnal changes in the p_H of the sap due to light changes are reflected in variations of the proportion of soluble iron. Translocation of iron occurs principally in the xylem and precipitation, which takes place over a wider p_H-range than in purely inorganic systems, is most marked in tissues of high p_H lying adjacent to others of low p_H. In plants whose tissues have a low and fairly uniform p_H, precipitation of iron is small and the element remains evenly distributed throughout all tissues. The parallelism between high iron contents and high acidity in pear sap is also recorded by J. Oserkowsky,[33] who observes that these conditions are most marked in the early part of the growing season, but the period of high acidity is prolonged after the seasonal decrease in iron content commences. It is also significant that among trees of the same orchard there is no appreciable difference in the p_H or iron content of the sap of normal and chlorotic branches. In an examination of sap from mulberry leaves, Y. Imamura and M. Furuya[34] indicate the nature of the gradient in sap concentration in various cell layers, *viz.*, upper epidermis > lower epidermis > spongy parenchyma > palisade tissue. The sap concentration generally, increases with the age of the leaves up to maturity and subsequently declines. Changes in the sugar content of saps corresponding with alterations in physiological activity are recorded by a number of workers. R. C. Cole[35] records greater proportions of glucose than of sucrose in stems and leaves of potato plants. Regular diurnal changes took place in the glucose concentration, but the sucrose content remained at approximately the same level throughout the day. The total sugar content increased with growth, but was not directly affected by the manurial treatment of the soil. Fertiliser applications, however, definitely influence the mineral constituents of sap, there being a general tendency to associate higher sap concentrations with higher proportions of the respective ions in the soil. A somewhat unexpected instance is, however, recorded by N. A. Pettinger,[36] working with maize. Fertilisers containing chloride increased the chloride concentration of the sap to a considerable extent, the effect being persistent for a long period of time. Sulphate-containing fertilisers, however, caused little, if any, change in the proportion of sulphate in the sap. An association between the crop-producing power of vines and the sap concentration of carbohydrate and asparagine at the period when buds are breaking is shown to exist by L. Moreau and E. Vinet,[37] and the relationship is confirmed by the fruit yield increase, following artificial injection of glucose into the stems immediately prior to the budding period.

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[30] *Plant Physiol.*, 1932, **7**, 261; *A.*, 1180.

[31] *Biochem. Z.*, 1932, **247**, 35; *A.*, 785.

[32] C. H. Rogers and J. W. Shive, *Plant Physiol.*, 1932, **7**, 227; *A.*, 1181.

Changes in, and Distribution of Certain Plant Constituents.

Climate and the Nature of Plant Substances.—Reference should be made here to a series of papers by J. B. McNair[38] in which are traced relationships between the chemical composition and, in some cases, physical properties of the principal plant constituents, and the environmental conditions of growth. Thus the acid-, alcoholic-, ester-, and hydrocarbon-constituents of volatile oils, saponins, and carbohydrates from plants occurring in temperate regions have, in general, higher molecular weights than those from tropical plants. Dextrorotatory compounds are more general in the volatile oils of temperate-region plants, and lævorotatory in tropical plants. Among saponins, those of tropical areas are the less toxic. Acetone is more common among the products of hydrolysis of cyanogenetic glucosides of temperate zones, and benzaldehyde among those of tropical plants. Nearly all plants containing cyanogenetic glucosides also contain calcium oxalate depositions, but in temperate plants the trihydrated and in tropical plants the monohydrated crystals predominate. Temperate-plant starches are the more reactive and have wider ranges of polarisation values and lower gelatinisation temperatures and are less "saturated" towards iodine than tropical starches. Essential oils, resins, and calcium oxalate crystals are far more commonly found in tropical than in temperate plants. The essential oils and resins occur in most cases in similar anatomic structures and there is a general tendency for resins to be formed by the condensation or polymerisation of the constituents of the essential oils.

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[33] C. H. Rogers and J. W. Shive, *Plant Physiol.*, 1932, **7**, 253; *A.*, 1180.

[34] *Bull. Sericult. Silk Ind. Japan*, 1932, **4**, 7; *A.*, 977.

[35] *Soil Sci.*, 1932, **33**, 347; *B.*, 697.

[36] *J. Agric. Res.*, 1932, **44**, 919; *A.*, 1181.

[37] *Compt. rend. Acad. Agric. France*, 1932, **18**, 193; *B.*, 362.

[38] *Amer. J. Bot.*, 1931, **18**, 416; 1932, **19**, 168, 255, 518; *A.*, 99, 663, 665; also *Science*, 1932, **76**, 83; *A.*, 1177.

Similar relationships are traced among plant waxes and alkaloids, although these are perhaps a little less clearly defined.

It is further recorded by S. Ivanov [39] that plant fats from northern areas always contain a larger proportion of unsaturated glycerides than those from southern areas, except among those containing oleic acid, in which a climatic influence is not appreciable. Other general relationships of a similar nature are shown by the work of N. N. Ivanov.[40]

Nitrogenous Constituents.—Among investigations of factors influencing the transformation of nitrogen compounds in plants interest attaches to that of S. H. Eckerson,[41] who traces the effects of nutrient deficiencies on the reduction of nitrates. Reducase activity, while largely influenced by light conditions, practically ceased in plants deficient in potassium or phosphate. Calcium or sulphate deficiency produced a similar effect but much more slowly. In the case of sulphate deficiency there is a tendency for the maintenance of a minimum rate of reduction over a period of some weeks.

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[39] *Chem. Rund. Mitteleuropa Balkan*, 1930, **7**, 115; *A.*, 1931, 535; also N. N. Ivanov, M. N. Lavrova, and M. P. Gapochko, *Bull. appl. Bot. Russia*, 1931, **25**, 1; *A.*, 1932, 663.

[40] *Biochem. Z.*, 1932, **250**, 430; *A.*, 1181.

[41] *Contr. Boyce Thompson Inst.*, 1932, **4**, 119; *A.*, 890.

Regulation of protein metabolism is examined by K. Mothes,[42] who has isolated from the onion an active substance which under reducing conditions stimulates protease activity and under oxidising conditions inhibits it. The material is rich in amino-acid constituents, when reduced responds to the nitroprusside test for the thiol group, and is probably glutathione or a closely related substance. T. Schulze[43] also records the isolation by a similar process of a cystine-like substance which influences proteolytic activity in leaves in a similar manner to the above. The view is also expressed that the protein balance in leaves is such as to maintain a characteristic "stability value" of protein per unit dry weight or per unit surface area of leaf. Hydrocyanic acid from cyanogenetic glucosides activates protein exchange. Following up earlier investigations,[44] G. Klein and his colleagues[45] have examined the distribution of urea in plants. In the higher plants a large proportion of urea exists in the form of ureides (probably of aldehydes), but in many fungi free urea predominates. In the former urea appears to result from the destruction of arginine by enzymes. The same author, applying his recently developed methods of analysis, examines the distribution of choline in plants, especially in seedlings.[46] The choline contents of fresh seeds is small, leguminous seeds containing more than others. During the germination of maize lecithin- and free-choline (especially the latter) increase considerably, the preponderance of lecithin-choline appearing in the cotyledons. Etiolated seedlings have more free choline and less lecithin-choline than normal. Nitrogen exchange in seedlings is also examined by P. McKie,[47] who observes a close relationship between the disappearance of insoluble- and protein-nitrogen during germination of lupin seeds and the increased proportion of asparagine. Later, as the seedling becomes established, protein synthesis begins and there occurs a decline in the amount of asparagine and a corresponding increase in proteose. The simpler forms of nitrogen, nitrate, ammonia, amides, and amino-acids appear immediately growth begins and after maintaining a maximum value for a few days decline to a low maintenance level. In germinating soya beans[48] the initial protein decomposition results in the production of ammonia and urea. Subsequent changes in the seedling are due to the action of proteases on glycinin. The urease activity of seedlings is greater than that of the seeds.

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[42] *Naturwiss.*, 1932, **20**, 102; *A.*, 436.

[43] *Planta* [*Z. wiss. Biol.*], 1932, **16**, 116; *A.*, 549.

[44] *Jahrb. wiss. Bot.*, 1930, **73**, 174; *A.*, 1931, 990.

[45] *Ibid.*, 1931, **74**, 429; *A.*, 1932, 313; *Biochem. Z.*, 1931, **241**, 413; 1932 **251**, 10; *A.*, 1932, 101, 313, 1179.

[46] G. Klein and H. Linser, *Biochem. Z.*, 1932, **250**, 220; *A.*, 1179.

[47] *Biochem. J.*, 1931, **25**, 2181; *A.*, 1932, 202.

[48] W. S. Tao and S. Komatsu, *Mem. Coll. Sci. Kyoto*, 1931, **14**, 287, 293; *A.*, 1932, 202.

Seasonal variations in the nitrogen distribution in fruit trees have again received attention. A. S. Mulay [49] continues his examination of Bartlett pear shoots.[50] Among the non-protein nitrogenous constituents of current-year shoots, amides and amino-acids in both wood and bark reach a maximum prior to the commencement of new growth. During growth the amide-nitrogen of the wood exceeds the amino-nitrogen. Basic-nitrogen is low at mid-summer, but subsequently rises to attain a maximum some time before new growth begins. The insoluble-nitrogen of bark and wood is also examined. In the bark small increases in amide- and humin-nitrogen at the expense of basic- and residual-nitrogen occur in the early growing season and later there is a decrease in amino-nitrogen and a corresponding rise in residual-nitrogen as growth proceeds. The principal changes in the wood are shown in a considerable decline in amino-nitrogen and an increase in melanin. Residual nitrogen increases somewhat after the actual cessation of growth. Similar though perhaps rather less detailed examinations of apple trees are recorded by J. T. Sullivan and H. R. Kraybill [51] and by A. E. Murneek and J. C. Logan.[52] The nitrogen and carbohydrate metabolism of celery plants is examined by H. Platenius.[53] During growth there is an inverse relationship between the nitrate- and the amino-nitrogen contents and between the amino- and protein-nitrogen. The proportion of ammonia in the plants was consistently small. Temperature changes had little effect on the rate of amino-acid synthesis. Relationships between metabolic changes and the premature seeding of celery are discussed.

Carbohydrates in Plants.—Apart from papers dealing with purely systematic chemistry, a relatively small number of investigations fall to be reported here. H. Belval [53a] discusses the process of sugar formation in leaves and from a consideration of the wheat plant indicates that in leaves sucrose formation precedes that of the simple hexoses. A fructoside is also formed from sucrose. Sucrose is also the first recognisable sugar formed in the banana leaf. Wheat stems differ from those of maize and rice by the presence, along with glucose and fructose, of an alcohol-soluble non-reducing lævorotatory sugar other than sucrose. From the roots of *Lycoris squamigera*

[49] *Plant Physiol.*, 1932, **7**, 107, 323; *A.*, 436, 1180.

[50] *Ann. Reports*, 1931, **28**, 251.

[51] *Proc. Amer. Soc. Hort. Sci.*, 1931, **27**, 220; *A.*, 1932, 99.

[52] *Missouri Agric. Exp. Sta. Res. Bull.*, 1932, No. 171.

[53] *Cornell Univ. Agric. Exp. Sta. Mem.*, 1932, No. 140; *A.*, 1295.

[53a] *Bull. Soc. d'Encour.*, 1931, 130, 605; *A.*, 1932, 100; see also *Chinese J. Physiol.*, 1930, **4**, 365; *A.*, 1931, 130.

Belval has isolated two fructosides, one of which, *lycoroside*, ($C_{48}H_{80}O_{40}$), $[\alpha]$ − 34°, is not hydrolysed by invertase and the second [54] has $[\alpha]$ − 19° and is slowly hydrolysed by the enzyme. Carbohydrate changes during seed formation in peas show varietal differences in the period of formation of stachyose.[55] In one case appreciable amounts of sucrose with reducing sugars but no stachyose were present initially. With the development of starch accumulation reducing sugars disappeared, sucrose decreased in amount, and stachyose appeared only in the later stages. In a second variety the formation of stachyose and of starch occurred simultaneously. Significant differences in the carbohydrate exchange of sterile and of inoculated soya beans are recorded by E. Rüffer.[56] In the early stages of growth the greater assimilation by inoculated plants resulted in relatively greater accumulations of sugars and starch, which were subsequently reduced below the level of sterile plants, presumably as a result of utilisation by the nodule organisms. In the carbohydrate metabolism of *Crassuluceæ*, J. Wolf [57] shows that the carbohydrate consumption is not exactly balanced by the formation of malic acid and carbon dioxide. It is considered that high concentrations of carbon dioxide in the tissues reduce decomposition by inhibiting the first stage of oxidation (oxalacetic acid formation) and also by causing an increased acetaldehyde accumulation, which in turn restricts the decomposition of α-ketonic acids by carboxylase.[58]

Carbohydrate and other changes during the ripening and storage of fruits. In the development of apples, starch formation commences (in this country) about mid-June and after reaching a maximum stage (July–August) the starch content declines steadily until the end of October. In apple tissue there exist a hydrolysable polysaccharide other than starch or pectin and a polyuronide. Both substances yield arabinose on hydrolysis and are classed as hemicelluloses.[59] Hemicelluloses do not act as reserve carbohydrates, but resemble pectin in structure and function. In peaches, G. T. Nightingale, R. M. Addoms, and M. A. Blake [60] show that pectates are absent from the flesh cells during ripening and are only to be found in the thick-walled cells adjacent to the epidermis. Protopectin, although irregularly distributed, occurs in all cell walls and is closely associated with cellulose. In the soft ripe stage there is a gradual decline in the protopectin content. The ripening of the Japanese medlar is associated with an accumulation of fructose, sucrose, and malic acid in, and the disappearance of maltose, tartaric acid, and amygdalin from, the pericarp. With advancing ripening, dextrin, starch, cellulose, hemicellulose, protein- and non-protein-nitrogen decline steadily in amount. Changes of the reverse type occur simultaneously in the seed, where amygdalin, starch, cellulose, and hemicellulose increase in proportion and maltose disappears.[61] R. Nuccorini [62] in confirmation of earlier work [63] records differences in the distribution of organic acids in ripe cherries, peaches, and plums according to the period of ripening. In general, the proportion of malic acid formed during ripening is smaller, and that of tartaric acid greater, in warmer than in colder seasons. Characteristics of ripening oranges recorded by P. R. v. d. R. Copeman [64] include a steady increase in total solids and sugars and a decrease in the acids of the juice and also a decrease in the proportion of cell-wall material in the pulp. The interesting observation is also made that spraying with lead arsenate induced a definite decrease in the acid and a slight decrease in the sucrose (but not reducing sugar) content of the juice and also a significant increase in the proportion of cell-wall material in the pulp. The sugar that accumulates during the colouring period of fruit is considered by E. W. Allen [65] to consist mainly of sucrose in stone fruits, sucrose *plus* reducing sugars in apples, and reducing sugars in pears. During the storage of apples there occurs an inversion of sucrose and hydrolysis of starch, if any is present. Sucrose inversion and sugar oxidation do not always take place at parallel rates. Differences in hexose content thus brought about were shown in fructose but not in glucose, which remained in almost constant proportions. Storage also involves a steady loss of acid and of insoluble matter. The extent of the above changes varies somewhat with the period of picking. Generally speaking, late gathering results in a low rate of total-sugar loss, a high rate of sucrose inversion, a higher level of concentration at which sucrose inversion ceases, and wider variations in the content of reducing sugars.[66] Artificial ripening induced by treatment with ethylene appears to follow the normal course in respect of acid and carbohydrate changes in so far as these have been investigated,[67, 68, 69, 70] although the changes involved vary considerably with conditions of treatment, period of picking, and individual varieties. Treatment with acetylene [71] has similar effects.

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[54] *Compt. rend.*, 1931, **193**, 891; *A.*, 1932, 202.
[55] M. Bridel and C. Bourdouil, *ibid.*, p. 949; *A.*, 1932, 100.
[56] *Z. Pflanz. Düng.*, 1932, **24A**, 129; *A.*, 1180.
[57] *Planta* [*Z. wiss. Biol.*], 1931, **15**, 572; *A.*, 312.
[58] See also K. Wetzel and W. Ruhland, *ibid.*, p. 567; *A.*, 312.
[59] E. M. Widdowson, *Ann. Bot.*, 1932, **46**, 597; *A.*, 1070.
[60] *New Jersey Agric. Exp. Sta. Bulls.*, 494 and 507; *A.*, 1931, 273.

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[61] A. L. Kurssanov, *Planta* [*Z. wiss. Biol.*], 1932, **15**, 752; *A.*, 435.

[62] *Ann. Chim. Appl.*, 1932, **22**, 10; *A.*, 435.

[63] *Ibid.*, 1930, **20**, 302; *A.*, 1930, 1482.

[64] *Trans. Roy. Soc. S. Africa*, 1931, **19**, 107; *A.*, 1931, 882.

[65] *Hilgardia*, 1932, **6**, 381; *A.*, 975.

[66] H. K. Archbold, *Ann. Bot.*, 1932, **46**, 407; *A.*, 1070.

Anthocyanins.—Reference must be made here to the valuable work of Mrs. G. M. Robinson and R. Robinson. Detailed consideration of the synthesis of anthocyanin pigments [72] and the examination of their distribution in a vast number of plants [73] are beyond the scope of this section of the Report. The simplest type of anthocyanin is represented by chrysanthemin (cyanidin 3-monoglucoside), which forms the basis of consideration for the structure of more complex types. Pelargonin, pæonin, cyanin, and malvin conform to a 3 : 5-di-monoside type and are not classed as biosides. Among 3-biosides are included mecocyanin, prunicyanin, etc. No evidence of the existence of 5-monosides has been obtained.

Colour variations, especially among varieties of the same species of plants, are not ascribed to variations in the p_H of saps but depend upon differences in the nature of " co-pigments," *i.e.*, substances forming weak addition compounds with the anthocyanin and effecting a modification of colour. Such additive compounds usually dissociate at high temperatures or may be separated by partition between solvents. Co-pigmentation appears to be most marked in natural pigments containing anthoxanthins. Commonly occurring co-pigments include tannin, flavone, and flavonol glycosides. The existence of tannin complexes is also recorded by A. Guilliermond,[74] who indicates the oxyflavonols as precursors of anthocyanins in flowers of *Iris germanica.* The rate of formation of anthocyanin pigment in plants appears to vary with the growth rate, the photosynthetic activity, and the accumulation of nutrient substances.[75] In green fruit during chlorophyll assimilation the formation of anthocyanin is retarded owing to the production of anthocyanidins from the corresponding oxyflavones. In picked unripe fruit, reduction processes prevail and flavone compounds are converted

[67] W. B. Davis and C. G. Church, *J. Agric. Res.*, 1931, **42**, 165; *A.*, 1931, 774.

[68] E. H. Kohman, *Ind. Eng. Chem.*, 1931, **23**, 1112; *B.*, 1932, 79.

[69] F. W. Allen, *loc. cit.*

[70] H. S. Wolfe, *Bot. Gaz.*, 1931, **92**, 337.

[71] R. Hartshorn, *Plant Physiol.*, 1931, **6**, 467; *B.*, 1931, 992.

[72] *J.*, 1931, 2665—2742; 1932, 2221, 2293, 2299, 2488; *A.*, 1931, 1423; 1932, 1038, 1140; A. León, R. Robinson, *et al.*, *Anal. Fís. Quím.*, 1932, **30**, 267; *A.*, 859.

[73] *Biochem. J.*, 1931, **25**, 1687; 1932, **26**, 167; *A.*, 1932, 101, 1296.

[74] *Compt. rend.*, 1931, **192**, 1581; **193**, 112; *A.*, 1931, 1099.

[75] H. Kosaka, *J. Dept. Agric. Kyushu*, 1931, **3**, 29, 99; *A.*, 1931, 660; 1932, 101.

into anthocyanins.[76] In wheat and rye, but not in oats or barley, the anthocyanin colour is of sufficient intensity to be utilised as an indication of quality.[77]

Certain Plant Enzymes and their Artificial Activation.—The association of certain growth characteristics in plants with enzyme activity has become very general in recent years. Investigations of catalase activity are prominent, and in general indicate that this enzyme is most markedly active at the end of a period of dormancy or at the initiation of certain definite stages in growth, *e.g.*, during seed germination, sprouting of tubers, breaking of buds in fruit and other trees.[77a] Thus M. N. Pope [78] records maximum periods of activity in barley during early germination, during development of crown roots, and during early jointing.

A. Niethammer [79] correlates germinative capacity in seeds with their catalase content. Frost resistance in wheat plants appears to be related to the catalase activity of the leaf juices,[80] and in partially chlorotic leaves variations in catalase and in chlorophyll contents are closely parallel.[81] This association of functional with enzymic activity in plants is commonly reported in the case of amylase and other enzymes and much interest centres round this aspect of the artificial stimulation of growth processes and especially the interruption of the normal dormant period. The obvious horticultural value of such practice has doubtless been an incentive to numerous investigators. Probably the most widely examined activator is ethylene chlorohydrin. Potato tubers dipped in a 5% solution of this substance show a much accelerated sprouting and an increased number of sprouting eyes. This effect is greatest in least mature "seed." Subsequent growth, however, is greatest when well-matured tubers are treated.[82] The action of the activator decreases as the period of treatment approaches the end of normal dormancy. Similarly, ethylene chlorohydrin vapour breaks the dormancy of maple and chestnut seedlings [83] and of seeds of maples and oaks.[84] Treatment with certain sulphur-containing substances, *e.g.*, thiosemicarbazide, thioglycollic acid, methyl disulphide, thioglycol, and derivatives of thiocarbamic acid, is shown by L. P. Miller [85] to have a like effect on potato tubers. This stimulation of dormant material to active growth is associated in nearly all cases with a simultaneous increase in enzyme activity notably of catalase or amylase or both. Subsequently, numerous investigators have sought to decide whether enzyme activity is caused directly by the activator, or whether it is the indirect result of the action of the activator on other material, or whether the enzyme is actually a necessary intermediary between activator and growth response. Workers from the Boyce Thompson Institute have contributed a number of papers on this point. J. D. Guthrie [85a] shows that, among a number of activators examined, those inducing successful sprouting effects on potatoes either contained sulphur, or produced an increased proportion of thiol derivatives in the tuber as a result of an increased $p_{\rm H}$ or reducing power in the potato juice. Stimulative effects, however, are not closely correlated with changes in catalase or peroxidase activity nor with the $p_{\rm H}$ or reducing power of the juices. In a similar examination of gladiolus corms it is shown [86] that treatment with ethylene chlorohydrin increases the catalase and peroxidase activity and the thiol content of the expressed juice and of aqueous extracts of dried tissue. F. E. Denny [87] observes that sprouting response, while closely related to the increased amylase activity of the potato, is not directly dependent on the activation of the enzyme by ethylene chlorohydrin or thiocyanates. Later, J. D. Guthrie [88] reports the isolation of glutathione from the expressed juice of tubers treated with ethylene chlorohydrin but not from untreated tubers. The presence of glutathione in plant organs during active vegetative growth is also recorded in an examination of *Obelia* by E. J. Lund,[89] who reports maximum accumulations in the active tips of stems and roots. The distribution of glutathione in the plant is paralleled by variations in oxygen consumption, carbon dioxide production, methylene-blue reduction, and electric potential. L. Binet and J. Magrou [90] also regard the glutathione content of plants as a function of rapidity of growth. The direct activation of isolated amylase by various sulphur compounds is examined by R. H. Clark, F. L. Fowler, and P. T. Black.[91] Potassium thiocyanate, thiourea, and also ethylene chlorohydrin stimulate the action of malt diastase on starch, each activator exhibiting a specific optimum concentration giving maximum activity. H. Pringsheim, H. Borchardt, and H. Hupfer[92] show that glutathione activates both yeast and pancreatic amylases. Dithioglycollic acid, however, is without effect. Reduced glutathione resembles cystine in its activating action on proteolytic enzymes,[93] and it would appear that the activity of plant [and animal] cells is largely dependent on the S·S $\rightleftharpoons$ S·H equilibrium. Thus, while fairly definite knowledge has been obtained of the several factors involved in the activation of dormant plant tissue, the exact position of the enzymes as a causal or resultant factor in vegetative stimulation requires still further elucidation.

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[76] J. C. Politis, *Praktika*, 1928, **3**, 440; *A.*, 1932, 312.

[77] G. Gassner and W. Straib, *Pflanzenbau*, 1930, **4**, 169; *B.*, 1931, 507.

[77a] S. Manskaja and M. Schilina, *Biochem. Z.*, 1931, **240**, 276; *A.*, 1932, 99.

[78] *J. Agric. Res.*, 1932, **44**, 343; *A.*, 784.

[79] *Z. Pflanz. Düng.*, 1931, **21A**, 69; *B.*, 1931, 775.

[80] R. Newton and W. R. Brown, *Canadian J. Res.*, 1931, **5**, 333; *A.*, 1931, 1465.

[81] H. von Euler, *et al.*, *Arkiv Kemi, Min. Geol.*, 1931, **10B**, No. 13; *A.*, 1931, 1102.

[82] H. O. Werner, *Nebraska Agric. Exp. Sta. Bull.*, 1931, No. 57; *B.*, 1932, 318.

[83] W. C. Bramble, *Science*, 1932, **75**, 193; *B.*, 396.

[84] C. G. Deubner, *ibid.*, 1931, **73**, 320; *B.*, 1931, 857.

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[85] *Contr. Boyce Thompson Inst.*, 1931, **3**, 309; *B.*, 1931, 858.

[85a] *Ibid.*, p. 499; *A.*, 1932, 201.

[86] J. D. Guthrie, F. E. Denny, and L. P. Miller, *ibid.*, 1932, **4**, 131; *A.*, 889,

[87] *Ibid.*, p. 53; *A.*, 661.

[88] *J. Amer. Chem. Soc.*, 1932, **54**, 2566; *A.*, 889.

[89] *Protoplasma*, 1931, **13**, 236; *A.*, 1932, 98.

[90] *Compt. rend.*, 1931, **192**, 1415; *A.*, 1931, 989.

[91] *Trans. Roy. Soc. Canada*, 1931, [iii], **25**, III, 99; *A.*, 1932, 427.

Growth and Metabolism of Moulds.

Nutritional Factors.—The alleged parallelism between the production of mycelial tissue by *Aspergillus niger* and the supply of certain mineral nutrients, together with the utilisation of this organism as an indicator of the nutrient value of soils,[94] has lead to a number of investigations of the effect of inorganic materials on the growth of the mould. In soil analysis the many external influences on growth are stabilised as far as possible by the use of media containing 1% citric acid and any calcium carbonate in the soil is previously neutralised with citric acid. Extensive changes in the p_H of the nutrient are thus prevented. The proportion of soluble calcium in the nutrient nevertheless influences the growth of the organism[95] irrespective of the supply of potassium, and highly calcareous soils yield excessively high values for available potassium. Mycelium of *A. niger,* grown under conditions which make the supply of potassium a limiting factor, contains 0·12% (dry weight) of K_2O and production is closely proportional to the amount of this element available.[96] Correlation between mycelial growth and the phosphate supply is less close. This observation may be related, however, to the fact that *A. niger* is able to utilise, in addition to alkali and soluble calcium phosphates, the insoluble phosphates of iron and of calcium and also the phosphorus of phytin.[97]

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[92] *Biochem. Z.*, 1932, **250**, 109; *A.*, 1063; also *Naturwiss.*, 1932, **20**, 64; *A.*, 304.

[93] W. Grassmann, *et al.*, *Z. physiol. Chem.*, 1931, **194**, 124; *A.*, 1931, 393.

[94] H. Niklas, H. Poschenrieder, and J. Trischler, *Z. Pflanz. Düng.*, 1930, **18A**, 129; *B.*, 1931, 37.

[95] H. Niklas, G. Vilsmeyer, and H. Poschenrieder, *ibid.*, 1932, **24A**, 167; *B.*, 566.

[96] J. Trischler, *Wiss. Arch. Landw.*, 1931, **7**, 39; *B.*, 1932, 617.

[97] T. Simakova and G. Bovschik, *Z. Pflanz. Düng.*, 1932, **24A**, 341; *B.*, 743.

That mycelium production is also directly related to the magnesium supply is indicated recently.[98] The effect of heavy-metal salts on the growth of fungi, with its obvious bearing on industrial fermentation industries, has again been the subject of considerable investigation. J. Talts [99] has examined the acidity produced in media by the growth of *P. glaucum* and distinguishes two phases, *viz.*, an initial stage characterised by rapid tissue production and a marked increase in hydrogen-ion concentration, followed by a second stage in which the growth rate is smaller and acidity diminishes. Salts of zinc, cobalt, nickel, and cadmium in $0{\cdot}005M$-solutions markedly affect the p_H changes in the medium and are toxic in the order Ni<Zn<Co<Cd. Toxicity is ascribed to a retardation of absorption of nutrients rather than to coagulation of the colloids of the plasma, and is associated with reduced spore germination. The effect of zinc sulphate on the growth of *A. niger* is also examined by K. B. Stehle.[99a] Stimulation by small concentrations of zinc occurs only when the sugar in the nutrient is above a definite proportion and does not appear if starch or inulin is supplied instead of sugar. The addition of a colloid (agar-agar) prevents the stimulative action of small concentrations of zinc and protects the fungus from the toxic effects of larger ones. According to R. A. Steinberg [1] zinc is to be regarded as an essential nutrient for *Aspergillus* rather than as a stimulant. The apparently irregular action of iron in the culture of fungi is emphasised and discussed by A. Quilico and A. Di Capua,[2] who record the isolation of two strains of *A. niger*, one of which gave hardly any citric acid in the presence of traces of iron, and a second which produced citric acid in proportion to the amount of ferric chloride supplied. The presence of cellulosic material also influences the growth of this organism, additions to the medium of filter paper, washed peat, powdered barley roots, etc., markedly increasing the amount of mycelium produced.[3]

Metabolism and Acid Production.—Gaseous exchange in *A. oryzæ* is examined by H. Tamiya,[4] who records the view that the respiratory quotient is greater or less than the combustion quotient of the substrate according to whether the latter is greater or less than

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[98] H. Niklas, H. Poschenrieder, and A. Frey, *Ernähr. Pflanze*, 1931, **27**, 465; *B.*, 1932, 276.

[99] *Protoplasma*, 1932, **15**, 188; *A.*, 968.

[99a] *Bull. Torrey Bot. Club*, 1932, **59**, 191; *A.*, 1168.

[1] *Zentr. Bakt. Par.*, 1932, II, **86**, 139; *A.*, 1168.

[2] *Giorn. Chim. ind. appl.*, 1932, **14**, 289; *A.*, 968.

[3] L. E. Kiessling, *Z. Pflanz. Düng.*, 1931, **21A**, 86; *B.*, 1931, 774; *Pflanzenbau*, 1932, **9**, 293; *A.*, 1289.

[4] *Acta Phytochim.*, 1932, **6**, 227, 265; *A.*, 1167.

0·875 (the combustion quotient of the mould constituents taken as a whole). Energy resulting from respiration during vital synthesis appears to be utilised for the maintenance of enzymic and structural energy, balancing heat exchanges in various stages of synthesis, and for activation of the substrate for the acceleration of synthetic reactions. Following up earlier work, the same author records the manner of utilisation of a large number of organic substances for growth and/or respiratory purposes, and associates certain specific atomic groupings with their utilisation by the mould.[5] It would appear that the presence of more than one specific grouping is necessary for growth. Typical "chief radicals" include the groups $\cdot CHMe(OH)$, $\colon CH\cdot C(OH)\colon$, and $\cdot CH(OH)\cdot CH_2\cdot$. These must be joined at least once with a "residual radical" such as will prevent β-degradation and fission of the "chief radical." Fission of di- and poly-saccharides and of glucosides precedes their utilisation. The utilisation, as sole source of carbon, of the higher paraffins by a strain of *A. versicolor* is recorded by S. J. Hopkins and A. C. Chibnall.[6] Both odd- and even-paraffins up to $C_{34}H_{70}$ are attacked, and also higher ketones but not secondary alcohols. Contrary to the view of W. O. Tausson,[7] the first products of the action on paraffins appear to be ketones, which gives rise subsequently to shorter-chain fatty acids. K. Bernhauer and his colleagues,[8] in a continuation of their investigations of the various acids produced by *A. niger*, show that glycollic acid produced from acetates is rapidly replaced in cultures by glyoxylic acid as the action proceeds. Both acids may be converted into oxalic acid. Quantitative examination of the process in comparison with the conversion of succinates into oxalic acid leads to the view that acetic acid is transformed into oxalic acid by way of succinic rather than through glycollic acid. In the conversion of ethyl alcohol into citric acid by *A. niger* the simultaneous production of oxalic, malic, and tartaric acids is also recorded.[9] The yield of citric acid is greater and that of oxalic acid smaller than the corresponding amounts formed from acetates. According to T. Chrzaszcz, D. Tiukov, and M. Zakomorny [10] the conversion of alcohol into citric acid by *Penicillium* takes place through the stages, alcohol ⟶ acetic ⟶ glycollic ⟶ *l*-malic ⟶ citric acids. The extent of the side reaction, glycollic ⟶ oxalic acid, varies with the strain of organism used and with the nature of the substrate. In another paper dealing with this point T.

[5] *Acta Phytochim.* 1932, **6**, 129; *A.*, 651.

[6] *Biochem. J.*, 1932, **26**, 133; *A.*, 653.

[7] *Biochem. Z.*, 1928, **193**, 85; *A.*, 1928, 447.

[8] K. Bernhauer and Z. Scheuer, *ibid.*, 1932, **253**, 11; *A.*, 1168.

[9] K. Bernhauer and N. Böckl, *ibid.*, p. 25; *A.*, 1168.

[10] *Ibid.*, **250**, 254; *A.*, 1065.

Chrzaszcz and D. Tiukov [11] show that for maximum accumulation of citric acid there is an optimum concentration of nitrogen in the medium which depends on the form of the nitrogen. For inorganic forms of nitrogen the optimum is lower than for organic forms. Further, some moulds produce citric acid by deamination without the production of oxalic acid. Considerable yields of acetaldehyde produced from sucrose by *A. niger* in media containing sodium sulphite are recorded by K. Bernhauer and H. Thelen.[12] It is significant that neither citric nor oxalic acid is formed under these conditions, but both are produced in the absence of sodium sulphite. The formation of itaconic acid by a new organism, *A. itaconicus*, grown on a sucrose–potassium nitrate medium is of interest. The change probably occurs in the order, sugar ⟶ gluconic acid ⟶ citric acid ⟶ aconitic acid ⟶ itaconic acid. The same organism, grown on sucrose–ammonium nitrate, produces *l*-mannitol. Fructose (but not glucose) undergoes similar changes.[13]

Among benzene derivatives obtained by the action of moulds on glucose must be mentioned puberulic acid, $C_8H_6O_6$, m. p. 316° (decomp.), probably a dihydroxybenzenedicarboxylic acid, and an acid, $C_8H_4O_6$, m. p. 296° (decomp.), not characterised. The acids are produced by *Penicillium puberulum*, Bainier, and *P. aurantio-virens*, Biourge, when supplied with glucose as the sole source of carbon.[14] The course of the degradation, quinic acid ⟶ protocatechuic acid ⟶ pyrocatechol ⟶ oxalic acid by *A. niger* is examined by K. Bernhauer and H. H. Waelsch,[15] who demonstrate the disappearance of pyrocatechol on the 6th day of the culture, but the appearance of oxalic acid is not shown until the 9—10th day. Oxalic acid is similarly produced from inositol, gallic, and salicylic acids. Oxalic acid appears to be the only acid produced by *A. niger* from potassium salts of *d*-glycuronic, α-*d*-galacturonic, and tetragalacturonic acids.[16] An extensive survey of the production of a number of organic acids by modern fermentation processes is given by O. E. May and H. T. Herrick.[17] The utilisation of olive oil by *A. flavus* and *P. sylvaticum* is reported by R. S. Katznelson [18] and of linseed and walnut oils by H. Oeffner.[19] In the latter instances evidence of the formation of γ- and δ-hydroxy-acids and their lactones is given. Intermediate products include certain unsaturated compounds.

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[11] K. Bernhauer and N. Böckl, *Biochem. Z.*, 1931, **242**, 137; *A.*, 1932, 93.

[12] *Ibid.*, 1932, **253**, 30; *A.*, 1168.

[13] K. Kinoshita, *Acta Phytochim.*, 1931, **5**, 271; *A.*, 1932, 93.

[14] J. H. Birkinshaw and H. Raistrick, *Biochem. J.*, 1932, **26**, 441; *A.*, 651.

[15] *Biochem. Z.*, 1932, **249**, 223; *A.*, 882.

[16] E. Hoffman, *ibid.*, 1931, **243**, 423; *A.*, 195.

[17] *Chem. News*, 1932, **145**, 81; *A.*, 968.

[18] *Arch. Sci. biol., Russia*, 1931, **31**, 385; *A.*, 1932, 1168.

[19] *Bot. Archiv*, 1931, **33**, 172; *A.*, 1932, 93.

Examination of fungal mycelium reveals differences in carbohydrate composition which are related to the nature of the nutrient. Thus on a glucose substrate *A. niger* contains a high proportion of trehalose and a small amount of mannitol. On media containing invert sugar or fructose the proportions are reversed.[20] Mannitol is also present in the mycelium of *A. fischeri* and *A. oryzæ*. The production of ergosterol by these organisms [21] and by *P. puberulum* [22] is also recorded.

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[20] Obaton, *Compt. rend. Soc. Biol.*, 1930, **105**, 673; *A.*, 1932, 651.

[21] L. M. Pruess, W. H. Peterson, and E. B. Fred, *J. Biol. Chem.*, 1932, **97**, 483; *A.*, 1065.

[22] J. H. Birkinshaw, R. K. Callow, and C. F. Fischmann, *Biochem. J.*, 1931, **25**, 1977; *A.*, 1932, 195.

GEOCHEMISTRY.

GENERALLY speaking, the period under review has been one of steady advance in all the branches indicated in the Report for 1930. Perhaps the most important development lies in the increasing application of chemical principles to the description of rocks and mineral deposits. There has been a very substantial output of physicochemical data for the oxide and other systems, so that many problems in igneous petrology, salt deposits, and ores can now be discussed in ordinary chemical terms. In this way the theory of chemical reactions in the earth's crust is assuming a more definite shape, and steps are being taken to avoid further extension of the earlier arbitrary descriptive terminology, which has been generally regarded as unsatisfactory. Many new minerals have been described; but an outstanding feature is the review of the principal mineral groups. Pyroxenes (Sundius, Barth), amphiboles (Winchell), tourmalines (Ward), zeolites (Hey), micas (Jakob), and other important divisions have been critically discussed, with many additional analyses.

In radioactivity, perhaps the most striking development is the consistent determination of the age of certain minerals, with consequent dating of the deposits in which they occur. Mineragraphic work includes descriptions of several famous ore-bodies, *e.g.*, the copper-bearing formation in N. Rhodesia; the mode of formation of the characteristic structures is being followed up, and the student now has the assistance of text-books such as the " Lehrbuch " of H. Schneiderhöhn and the " opaque minerals " bulletin of M. N. Short.

Formulation of the silicates continues to be discussed : in many cases new determinations of the unit cell contents have been made, but the interpretation is still troubled by uncertainty as to the extent of " proxy " substitutions : the spinels have been extensively studied, with results that fully establish the interchangeability of certain atoms. Another important discovery is the existence of atomic groups, such as O_3 in NH_4NO_3,[1] that appear to be capable of rotation; here the oxygens, like atoms in solid solution, are not directly represented by X-ray reflexions.

General Geochemistry.

Spectroscopic studies have been made of the Katzenbuckel rocks by F. Schröder,[1a] and of tourmaline, diopside, and rocksalt by G. O. Wild.[2] In coloured minerals the absorption spectrum changes with the direction of vibration; many minerals, especially those with uranium have been studied by B. Lange and W. Eitel,[3] and by F. Corin.[4]

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[1] *J. Amer. Chem. Soc.*, 1932, **54**, 2766.

[1a] *Jahrb. Min.*, 1931, [*A*], **63**, 215; *A.*, 595.

Several new devices have been proposed for density work. W. Kratschmai [5] has designed a new balance of Westphal type, but giving direct readings for density. A similar instrument by G. Scharffenberg [6] has a circular beam with very widely separated knife edges. New separating vessels for the centrifuge are given by W. Kunitz [7] and H. Müller; [8] for heavy liquids by S. Klein.[9] J. L. Rosenholz and D. T. Smith [10] have prepared tables for specific gravity and hardness of minerals. Piperine, *n* 1·68, is recommended as a mounting medium by J. H. Martens.[11]

M. M. Stephens [12] finds that some silver minerals may be etched with a powerful arc-light. For mineragraphy an important set of tables has been compiled by M. N. Short,[13] in a form similar to the well-known tables for non-opaque minerals by E. S. Larsen; colour, hardness, anisotropy and etching properties are listed for the opaque ores, with a section on micro-reactions. Another important contribution is the second edition (much extended) of the " Lehrbuch der Erzmikroskopie " by H. Schneiderhöhn and P. Ramdohr (Berlin, 1931), supplemented by " Erzmikroskopische Bestimmungstafeln " in a separate volume. M. Berek [14] and A. Cissarz [15] discuss the measurement of reflecting power. Microchemical analysis, both qualitative and quantitative, is described in F. Emich's " Mikrochemisches Praktikum " (Munich, 1931). Examples are given by H. Hueber.[16] A. N. Winchell's " Micro. characters of . . . artificial minerals " has been considerably enlarged in a second edition (New York, 1931). New minerals are listed, with brief descriptions, by L. J. Spencer [16a] in the " 12th list of new mineral names " and numerous physical data have been assembled by the same author.[17]

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[2] *Centr. Min.*, 1931, 254, 327, 430; 1932, 18; *A.*, 195.

[3] *Tsch. min. petr. Mitt.*, 1931, **41**, 435.

[4] *Ann. Soc. Sci. Bruxelles*, 1931, [*B*], **51**, 148; *A.*, 1931, 1145.

[5] *Centr. Min.*, 1932, 221, 348.

[6] *Ibid.*, p. 345.

[7] *Ibid.*, p. 225.

[8] *Ibid.*, p. 90.

[9] *Ibid.*, 1931, 244.

[10] *Rensselaar Poly. Inst.*, Eng. and Sci. Series, No. 34.

[11] *Amer. Min.*, 1932, **17**, 198.

[12] *Ibid.*, 1931, **16**, 532.

[13] *U.S. Geol. Survey*, Bull. 825, 1931.

[14] *Z. Krist.*, 1931, **76**, 396; *A.*, 1931, 587.

[15] *Ibid.*, 1932, **82**, 438.

[16] *Centr. Min.*, 1932, 337.

[16a] *Min. Mag.*, 1931, **22**, 614.

[17] " Annual Tables of Constants. . . ." Extracts from vol. 7 (special reprint) (Paris).

Much attention is now being given to the distribution of the elements in the earth's crust. V. M. Goldschmidt[18] and co-workers have produced a series of papers dealing with elements individually, such as gallium, boron, scandium, germanium (in coal). Tungsten in Bolivia[19] occurs mainly under lower temperature conditions than tin-ores. Vanadium has a remarkably wide distribution; it apparently accompanies titanium, and is present in small amounts in sea-sand and meteorites, in titanomagnetite and in volcanic rocks, as well as in sediments (up to 0·01%).[20] J. Papish and C. B. Stilson[21] find that gallium occurs in blende, galena, etc., but not in some other zinc minerals such as calamine, smithsonite, zincite.

General studies of the distribution of elements have been made by H. v. Kluber in "Das Vorkommen der chemischen Elemente im Kosmos" (Leipzig, 1931) for meteorites, planets, and stars. G. Berg's "Das Vorkommen der chemischen Elemente auf der Erde" inevitably covers in part the same ground as the series by V. M. Goldschmidt (above). Strontium has a specially interesting distribution; W. Noll[22] finds 0·1% (as oxide) in pyroxene and greater amounts in felspars.

Attention has been directed by H. S. Washington[23] to the possibility that beryllium has been overlooked and included as aluminium, with consequent errors in the comparison of norm and mode for rocks. C. Palache and L. H. Bauer[24] report berylla in vesuvianite (9·20%), cyprine, and barylite, also in milarite.

Many contributions have been made to the spinel problem, to which reference was made in an earlier report. W. Jander and W. Stamm[25] deduce from conductivity and diffusion measurements that some spinels are ionised while others show electronic conductivity. The form γ-Al_2O_3 has been studied by D. S. Beliankin and N. Dilaktorsky,[26] who find that its constants differ from those for Al_2O_3 dissolved in spinel. T. F. W. Barth and E. Posnjak[27] find further evidence for "variate atom equipoints"; see also F. Machatschki.[28] Atom size may be measured by "radius" (W. L. Bragg, V. M. Goldschmidt) or "space-filling" volume

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[18] *Nach. Ges. Wiss. Göttingen*, 1931, 165, *et al.*; *A.*, 39, 141, 248, 595, 926.

[19] F. Ahlfeld, *Chem. Erde*, 1932, **7**, 121; *A.*, 596.

[20] K. Jost, *ibid.*, p. 177.

[21] *Amer. Min.*, 1930, **15**, 521; *A.*, 1931, 817.

[22] *Naturwiss.*, 1931, **19**, 773; *A.*, 1931, 1391.

[23] *Amer. Min.*, 1931, **16**, 37.

[24] *Ibid.*, p. 469; *A.*, 1107.

[25] *Z. anorg. Chem.*, 1931, **199**, 165; *A.*, 1931, 999.

[26] *Centr. Min.*, 1932, 229.

[27] *J. Wash. Acad. Sci.*, 1931, **21**, 255; *A.*, 830.

[28] *Z. Krist.*, 1932, **82**, 348.

(T. W. Richards, J. J. Thomson [29]); W. Biltz [30] and others have carried out an extensive study of molecular and atomic volumes, mainly on an additive basis. G. Natta [31] has examined hydrogen chloride, bromide, etc., and finds relatively large atomic sizes for the halogens. It is interesting to recall that the original halogen volumes given by Wasastjerna depended on the experimental side on a small size assigned to hydrogen in the dissolved halide.

Oxide Systems.

G. W. Morey [32] has given a valuable discussion of silicate chemistry with many references to earlier literature on synthesis, particularly by the Geophysical Laboratory. Cr_2O_3 and Al_2O_3 form a continuous series of mix-crystals; and SiO_2–ZnO–Al_2O_3 (E. N. Bunting) yields Zn_2SiO_4,$ZnAl_2O_4$ and mullite, with bearing on the making of zinc-retorts.[33] Solutions of sodium chloride under pressure have been studied by L. H. Adams and R. E. Hall.[34] In MgO–$MgCl_2$–H_2O,[35] brucite yields, with $MgCl_2,6H_2O$ and solution, a magnesian cement. Many compounds in CaO–SiO_2–Al_2O_3–H_2O have been described in an extensive series of papers by S. Nagai,[36] both at atmospheric pressure and with high pressure and moderate temperature; sodium carbonate solution is used to separate the products. The same author, also W. Masgill, G. H. Whiting, and W. E. S. Turner,[37] have studied the silicates formed by heating chalk and silica. CaO–Na_2O–Al_2O_3 [38] yields two ternary compounds.

The volatility of silica in steam is discussed by G. W. Morey.[39] C. J. van Nieuwenburg and H. B. Blumendal [40] have volatilised silica in supercritical steam: kaliophilite is altered to leucite and orthoclase, while nephelite yields analcite and albite; carbon dioxide inhibits these reactions. Titanium and stannic oxides are not volatile under these conditions, but molybdenum and tungsten trioxides will react with lime to form $CaMoO_4$, etc.; copper is also volatile. Carbon dioxide under high pressure attacks the silicates reversibly.[41] K. Bito, K. Aoyama, and M. Matsui[42] find that calcium carbonate dissociates at about 915° under one atm. of carbon dioxide; fresh crystals require a slightly higher temperature. The system K_2O–CaO–SiO_2, important for glass-making, has been determined by G. W. Morey, F. C. Kracek, and N. L. Bowen,[43] and the behaviour of $K_2Si_4O_9$ under pressure has been investigated by R. W. Goranson and F. Kracek.[44]

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[29] *Phil. Mag.*, 1922, **44**, 657; **43**, 721. The sizes given by the "radius" method are often quite at variance with the "additive" volumes; cf. A. F. Hallimond, *Min. Mag.*, 1927, **21**, 277; 1928, **21**, 480; 1929, **22**, 70.

[30] *Z. anorg. Chem.*, 1932, **203**, 277, etc.

[31] *Mem. R. Accad. d'Italia*, 1931, **2**, 1.

[32] *Annual Survey of Amer. Chem.*, 1930, **5**, 457.

[33] E. N. Bunting, *Bur. Stand. J. Res.*, 1931, **6**, 946; 1932, **8**, 279; *A.*, 1931, 1010; 1932, 547.

[34] *J. Wash. Acad. Sci.*, 1931, **21**, 183; *A.*, 1931, 793.

[35] C. R. Bury and E. R. H. Davies, *J.*, 1932, 2008.

[36] *Z. anorg. Chem.*, 1932, **206**, 177, etc.

[37] *J. Soc. Glass Tech.*, 1932, **16**, 94.

[38] L. T. Brownmiller and R. H. Bogue, *Bur. Stand. J. Res.*, 1932, **8**, 289; *A.*, 574.

[39] *Geophys. Lab. Paper*, No. 786.

[40] *Rec. trav. chim.*, 1931, **50**, 989; *A.*, 1931, 1381.

Systems containing iron react with platinum vessels; in addition the two iron oxides react with the furnace gas. Complete success in these experiments has not yet been obtained, but a number of systems have been investigated over a considerable range of conditions. By using electrolytic iron crucibles in nitrogen, N. L. Bowen and J. F. Schairer[45] have explored the system ferrous oxide–silica. Ferric oxide appears, up to 11%, which diminishes sharply on addition of silica; all attempts to produce $FeSiO_3$ failed (although iron-rhodonite is common in slags). MgO–FeO–Fe_2O_3 in air at one atm. has been investigated by H. S. Roberts and H. E. Merwin;[46] equilibrium is attained slowly, and the alundum crucibles were protected by an adherent layer of the mixture; when homogeneous, the preparation was treated by the usual quenching method; one interesting feature is the formation of solid solutions not only between MgO,Fe_2O_3 and iron oxide but between that compound and magnesium oxide, a further contribution to the complex problem of the spinels. J. H. Andrew and W. R. Maddocks[47] describe solid solutions of FeS in Fe_2SiO_4.

The system potassium sulphate–water under pressure has been investigated by L. H. Adams.[48] G. Tunell and E. Posnjak[49] have compared the natural oxidation of sulphide ore-bodies with the behaviour of the system Fe_2O_3–CuO–SO_3–H_2O (part); goethite, tenorite, brochantite, antlerite, and $3Fe_2O_3,4SO_3,9H_2O$ were obtained. S. G. Lasky[49a] discusses the application of the phase rule to iron ores in limestone.

Several ternary compounds in Na_2O–B_2O_3–H_2O have been prepared by U. Sborgi;[50] CaO–FeO has also been studied by J. Konarzewski[51] with reference to Portland cement. Thermal data for silicates of Ca, Fe, Mg are given by W. A. Roth and H. Troitzsch,[52] also by H. Wagner.[53] V. A. Vigfusson[54] has prepared hydrated calcium silicates. Further data for gypsum–anhydrite are given by R. Nacken and K. Fill,[55] and also by L. Chassevent.[56] Lithiophilite ($LiMnPO_4$) has been prepared by F. Zambonini and L. Malossi[57] in phosphoryl chloride vapour. Phosphates related to the apatite group have been prepared by precipitation, as well as by heating at 1100°, by G. Trömel.[58] A. Sanfourche and J. Henry[59] note a false equilibrium in the action of water on $CaHPO_4$. Muscovite[60] has been prepared hydrothermally by heating the colloid mixture in a pressure bomb for 5 days at 300°.

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[41] W. Weyl, *Glastech. Ber.*, 1931, **9**, 641.

[42] *J. Soc. Chem. Ind. Japan*, 1932, **35**, 191.

[43] *J. Soc. Glass Tech.*, 1930, **14**, 149; 1931, **15**, 57; *A.*, 1931, 1011.

[44] *J. Physical Chem.*, 1932, **36**, 913.

[45] *Amer. J. Sci.*, 1932, [v], **24**, 177; *A.*, 997.

[46] *Ibid.*, 1931, **21**, 145; *A.*, 1931, 310.

[47] *J. Iron and Steel Inst.*, 1932 [adv. copy]; *A.*, 997.

[48] *J. Amer. Chem. Soc.*, 1932, **54**, 2229; *A.*, 810.

[49] *J. Physical Chem.*, 1931, **35**, 929; *A.*, 1931, 800.

[49a] *Econ. Geol.*, 1931, **26**, 485.

Petrology.

Rock analyses are very widely scattered in the literature, and it is impossible to deal with them adequately in the present Report. They are mainly intended for descriptive purposes, though a certain proportion of papers on the igneous rocks are accompanied by theoretical discussions on the mode of formation. A valuable text-book on petrology has been prepared by F. F. Grout: "Petrography and Petrology" (New York, 1932). The latter term is defined to include the discussion of theory, and the book will give the student a very clear account of the present state of speculation in this subject. Development has been hindered by a terminology which has not yet been successfully revised. Actually the total number of petrological terms to-day is about 1300,[60a] including not only all the rock names but the descriptive terms; with the progressive abandonment of a substantial proportion of the names, the list should reach manageable proportions. Throughout the work the student is assumed to have a fully competent knowledge of chemistry, physics, and mineralogy: there is a brief account of petrographical methods in the form of a series of problems, but the degree of condensation in this part of the book may be gathered from the paragraph dealing with rock-analysis: "Problem 6—To make a chemical analysis of a rock. Method—Refer to H. S. Washington. . . ." It may be some time before the painstaking student is free to attack Problem 7! The descriptions are mainly based on examples chosen from North American occurrences; evidence for the operation of the principal rock-forming processes has been clearly set out and the difficulties are not evaded. But again it must be emphasised that these chapters assume previous training, indeed there is some risk that so lucid a text-book may encourage a superficial acquaintance with "petrology" in students who lack the necessary groundwork of the older sciences.

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[50] *Gazzetta*, 1932, **62**, 3; *A.*, 341.

[51] *Rocz. Chem.*, 1931, **11**, 516, 607; *A.*, 1931, 1010, 1373.

[52] *Arch. Eisenhüttenw.*, 1932—1933, **6**, 79.

[53] *Z. anorg. Chem.*, 1932, **208**, 1.

[54] *Amer. J. Sci.*, 1931, [v], **21**, 67; *A.*, 1931, 310.

[55] *Tonind.-Ztg.*, 1931, **55**, 1194.

[56] *Compt. rend.*, 1932, **194**, 786.

[57] *Z. Krist.*, 1931, **80**, 442; *A.*, 38.

[58] *Z. physikal. Chem.*, 1932, **158**, 422; *Z. anorg. Chem.*, 1932, **206**, 227.

[59] *Compt. rend.*, 1932, **194**, 1940.

[60] W. Noll, *Naturwiss.*, 1932, **20**, 283.

[60a] A. Holmes, "The Nomenclature of Petrology," 2nd Ed. (London, 1928).

"Metamorphism" by A. Harker (London, 1932) will be an essential text-book for the more advanced student. Mineralogical changes produced by heating, chemical alteration, and pressure are systematically described, with many illustrative examples taken mainly from British occurrences. The development of porphyroblastic structures is traced with reference to the "crystallising power" of the mineral, which determines microstructures of a type quite distinct from those due to the crystallisation-sequence in igneous rocks. More than 200 drawings are very effectively used in place of photomicrographs.

Among numerous descriptions, mention may be made of papers by Romer,[61] who describes the gas, incrustations, and dacitoid lavas of Mt. Pelée. Liparite from the Crimea,[62] containing Fe 0·44, alk. 8·75%, might be used for glass manufacture. A. Holmes and H. F. Harwood [63] have given an extensive description of volcanic rocks from Uganda. Much discussion has recently centred upon the question how far an igneous intrusion can assimilate the wall-rocks: S. R. Nockolds [64] describes the process in a granite–greenstone contact from the Isle of Man; other instances are given by H. H. Thomas and W. Campbell Smith,[65] basic xenoliths in a Brittany granite; by H. C. Horwood,[66] granite–gneiss and granite–limestone contacts in Ontario; by L. A. N. Iyer [67] for granites in India; also a detailed study of granite slate contacts in Cornwall, by A. Brammall and H. F. Harwood.[67a] Differentiation without contamination has been studied by F. F. Osborne and E. J.

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[61] *Compt. rend.*, 1932, **195**, 393; *A.*, 1015.
[62] *Trans. State Inst. Test. Building Mat.*, 1930, **34**, 33.
[63] *Quart. J. Geol. Soc.*, 1932, **88**, 370; *A.*, 1015.
[64] *Min. Mag.*, 1931, **22**, 494; *A.*, 1931, 1029.
[65] *Quart. J. Geol. Soc.*, 1932, **88**, 274.
[66] *Trans. Roy. Soc. Canada*, 1931, [iii], **25**, IV, 227; *A.*, 359.
[67] *Rec. Geol. Surv. India*, 1932, **65**, 445; *A.*, 1107.
[67a] *Quart. J. Geol. Soc.*, 1932, **88**, 171; *A.*, 715.

Roberts,[68] who redescribe the Shonkin Sag laccolith ; by L. Jugovics,[69] for dacites in Bohemia ; and by A. Vendl,[70] for Hungarian andesites. E. Lehmann [71] derives basanite, trachyte, etc., in Nyassaland from a basaltic magma, and a similar explanation is given for basic flows in West Greenland.[72]

General theory includes a discussion of the earth's interior by A. A. Bless,[73] who estimates the temperature as 10^5 degrees, and rock-classifications by A. Johannsen [74] and E. Tröger.[75] A revision of the minerals postulated in calculating the " norm " of a rock has been proposed by T. F. W. Barth [75a] and criticised by C. E. Tilley.[76] P. Eskola [77] objects that the idea of a lighter sial layer is not supported by the frequent occurrence of granites in the pre-Cambrian, which rather indicates crystallisation-differentiation. Much attention has been given to the composition of the residual liquids formed during the crystallisation of a granite : C. N. Fenner [78] has pointed out that in some cases an increase in iron/magnesia ratio should occur, a fact which has not always been taken into account ; H. A. Powers [79] finds that in lavas from California the residual liquid was enriched in iron. A general theoretical discussion of this problem has been given by P. Niggli.[80] Experiments by R. W. Goranson [81] show that water, which becomes concentrated in the residue, has an important influence on the crystallisation of granite. Under 10 km. cover, a granite with 1% H_2O would begin to crystallise at 1025° ; at 700° the residual would contain 6·5% of water, and would continue to crystallise till below 500°, the result being 85% granite, 10% aplite, 5% quartz veins. Under only 4 km., the pressure will equal the hydrostatic head when the temperature falls to 950°, so that liquid can then be expelled from the reservoir ; this, the author considers, might result in the formation of two fluid phases.

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[68] *Amer. J. Sci.*, 1931, [v], **22**, 331 ; *A.*, 1931, 1265.

[69] *Tsch. min. petr. Mitt.*, 1932, **43**, 156 ; *A.*, 1107.

[70] *Ibid.*, 1932, **42**, 491.

[71] *Ibid.*, 1931, **41**, 8.

[72] H. Nieland, *Chem. Erde*, 1931, **6**, 591.

[73] *Proc. Nat. Acad. Sci.*, 1931, **17**, 225 ; *A.*, 1931, 816.

[7] " A Descriptive Petrography of the Igneous Rocks " (Chicago, 1931).

[75] *Jahrb. Min.*, 1931, [*A*], **62**, 249 ; *A.*, 1931, 1391.

[75a] *Tsch. min. petr. Mitt.*, 1931, **42**, 1 ; *A.*, 1931, 1391.

[76] *Ibid.*, 1931, **42**, 1 ; 1932, **43**, 68 ; *A.*, 926.

[77] *Ibid.*, 1932, **42**, 455 ; *A.*, 715.

[78] *Min. Mag.*, 1931, **22**, 539 ; *A.*, 1931, 1390.

[79] *Amer. Min.*, 1932, **17**, 253.

[80] *Rec. trav. chim.*, 1932, **51**, 633 ; *A.*, 829.

[81] *Amer. J. Sci.*, 1932, [v], **23**, 227 ; 1931, **22**, 483 ; *A.*, 492.

Radioactivity

Regular use is now being made of the Pb : U and other ratios for computing the age of rocks and minerals. C. N. Fenner [82] obtains 2779 × 10^5 years for the age of a monazite crystal, agreeing well with the value for uraninite from the same quarry. Thucholite gives 250 × 10^6 years,[83] while O. B. Muench [84] finds 373 × 10^6 years for cyrtolite from Bedford, N.Y., and 571 × 10^6 for that from Ontario. On the other hand, (Mlle.) E. Gleditsch and B. Qviller [85] report unduly low values for uranothorites. Kolm, the Swedish uranium-bearing shale, is proved by R. C. Wells and R. E. Stevens [86] to have an age of 458 × 10^6 years. G. Elsen [87] and (Mlle.) E. Gleditsch and S. Klemetsen [88] contribute to the investigation of actinium content. Lead in rocks is for the greater part not of radioactive origin.[89] A. Holmes [90] remarks that the total lead is from 4—50 times the generated lead; lead ores can have been derived from granitic magmas provided that the age of the earth is not more than 16 × 10^8 years. C. S. Piggot [91] gives data for the radium content of granites and of Hawaiian lavas. In granite the element is apparently chiefly associated with the micas.[92] Portuguese granites have yielded high radium values, and schists the lowest.[93] Lead may be included in crystals of sodium and potassium chloride; possibly it may occur in marine salts.[94] Natural waters sometimes contain radium,[94a] but it is largely eliminated by the presence of sulphate; water from petroleum wells, free from sulphate, had a higher radioactivity.[95]

Minerals.

Elements.—Few, if any, of the reported syntheses of diamond have survived further tests; M. K. Hoffmann [96] has repeated, with negative results, Hoff's synthesis by means of the carbon arc in liquid air E. Reuning[97] discusses the origin of the rich diamond deposits of S. W. Africa. Graphite is the subject of a monograph, "Der Graphit" by O. Kausch (Halle, 1931). Volcanic sulphur has been analysed by W. Geilmann and W. Biltz;[98] native sulphur occurs (inside oxidised pyrite concretions) in nacrous scales of the form S III, for which the name *rosickyite* is proposed by J. Sekanina.[99] Gold in the spathic veins of Siegerland occurs in pyrite as well as in bismuth minerals, representing two stages of the hydrothermal deposition.[1] Gold in jacutinga, according to E. de Oliveira,[2] is a secondary deposit from acid chlorine-bearing solutions due to oxidation of pyrite. In gravels gold has been reputed to "grow again" and F. W. Freise[3] shows that small amounts of humic acid in ground water will slowly dissolve gold in the absence of oxygen. Platinum[4] in the famous "Merensky horizon" is shown spectrographically to occur in the sulphides in solid solution; in dunite, where sulphides are deficient, the platinum is in the metallic form, associated with chromite; only the sulphide ores give rise to secondary platinum minerals on weathering. Several primary platinum ores are analysed by A. G. Betechtin;[5] Fe = 10—15%, also Cu, Ir, Ni. Osmiridium is shown by O. E. Zvjagintsev and B. K. Brunovski[6] to contain substantial amounts of ruthenium, rhodium, etc., all in solid solution. Native silver has been shown by (Sir) H. C. H. Carpenter and M. S. Fisher[7] to have a grain structure depending on the temperature of deposition or subsequent heating. At Konigsberg silver occurs largely in secondary forms; mercury, antimony, and nickel are present in some veins, which R. Støren[8] regards as of Temiskaming type. L. Tronstad[9] concludes that silver may be deposited at other points as well as the intersection of lodes with fahlbands. The genesis of the L. Superior copper–silver deposits is discussed by K. Nishio,[10] and by T. M. Broderick.[10a] E. B. Papenfus[10b] has described the "bedded" copper ores of Nova Scotia.

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[82] *Amer. J. Sci.*, 1932, [v], **23**, 327; *A.*, 595.

[83] A. Faessler, *Centr. Min.*, 1931, [*A*], 10; *A.*, 1931, 930.

[84] *Amer. J. Sci.*, 1931, [v], **21**, 350; *A.*, 1931, 594.

[85] *Phil. Mag.*, 1932, [vii], **14**, 233; *A.*, 1015.

[86] *J. Wash. Acad. Sci.*, 1931, **21**, 409; *A.*, 1931, 1391.

[87] *Chem. Weekblad*, 1931, **28**, 714; *A.*, 139.

[88] *Compt. rend.*, 1932, **194**, 1731; *A.*, 715.

[89] G. von Hevesy and R. Hobbie, *Nature*, 1931, **128**, 1038; *A.*, 139.

[90] *Ibid.*, p. 1039; *A.*, 139.

[91] *Amer. J. Sci.*, 1931, [v], **21**, 28; **22**, 1; *A.*, 1931, 332, 930.

[92] C. S. Piggot and H. E. Merwin, *ibid.*, 1932, [v], **23**, 49; *A.*, 139.

[93] G. Costanzo, *Rev. Chim. pura appl.*, 1931, [iii], **6**, 17; *A.*, 494.

[94] *Naturwiss.*, 1932, **20**, 86.

[94a] *E.g.*, J. L. Bohn, *J. Franklin Inst.*, 1930, **210**, 461; P. Forjaz, *Rev. Chim. pura appl.*, 1931, [iii], **6**, 15; J. A. Hootman, *Amer. J. Sci.*, 1931, [v], **22**, 453.

[95] W. Salomon-Calvi, *Petroleum*, 1931, **27**, 652; *A.*, 1931, 1145.

[96] *Centr. Min.*, 1931, 214.

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[97] *Jahrb. Min., Beil.-Bd.*, 1931, [*A*], **64**, 775; *A.*, 492.

[98] *Z. anorg. Chem.*, 1931, **197**, 422; *A.*, 1931, 816.

[99] *Z. Krist.*, 1931, **80**, 174; *A.*, 1931, 1390.

[1] J. M. Hüttenhain, *Tsch. min. petr. Mitt.*, 1932, **42**, 285; *A.*, 490.

[2] *Ann. Acad. Brasil. Sci.*, 1931, **3**, 151; *A.*, 829.

[3] *Metall u. Erz*, 1930, **27**, 442; *Econ. Geol.*, 1931, **26**, 421; *A.*, 1931, 1390.

[4] Siebert Festschr., 1931, 257.

[5] *Gorni Zhur.*, 1930, **106**, No. 1, 152; *A.*, 140.

[6] *Z. Krist.*, 1932, **83**, 172; *A.*, 1107.

[7] *Bull. Inst. Min. Met.*, 1932, No. 330; *A.*, 595.

[8] *Tidsskr. Kjemi Berg.*, 1931, **11**, 16; *A.*, 1931, 331.

[9] *Ibid.*, 1932, **12**, 15, 28; *A.*, 494.

[10] *Proc. World Eng. Congr.*, Tokyo, 1931, **37**, 499; *A.*, 596.

[10a] *Econ. Geol.*, 1931, **26**, 841.

[10b] *Ibid.*, p. 314.

Halides.—Salt domes are usually regarded as the result of the plastic flow of bedded salt deposits. In detail, however, they give rise to many difficult problems, such as the explanation of their association with petroleum, and the origin of the associated calcium sulphate and sulphur; these points are discussed by M. Stuart,[11] L. Owen,[12] and E. de Golyer.[13] Salt pans in Brazil form on the Permian outcrops and are of three types, containing nitrates, carbonates, and sulphates.[14] F. Heidorn [15] records magnesium fluoride with bitumen from the Zechstein. Radium fluoride is apparently present in isomorphous mixture in a radioactive fluorite described by F. L. Hess.[16] M. Kahanowicz [17] finds that blue fluorescence in sodium chloride is identical with that for metallic sodium, which has been suggested as the colouring matter. Halide phase-rule systems include that for (K, Na)Cl–H_2O, by E. Cornec and H. Krombach,[17] and the carnallite system by N. S. Kurnakow, D. P. Manoev, and N. A. Osokoreva.[18] G. Silberstein [19] describes "pipes" in limestone at Hopunvaara, with magnetite and fluorite in alternate layers.

Sulphides.—Stannite has been recorded from Tasmania,[20] Spain,[21] and from British Columbia; [22] these are of interest in connexion with the problem of cassiterite formation, and descriptions of Bolivian tin veins have been given by G. W. Lindgren and A. C. Abbott [23] (Oruro), F. Ahlfeld [24] (Uncia Llallagua), localities where the veins are related to dacitic intrusive rocks. R. Herzenberg [25] has described a new mineral *kolbeckin* (Sn_2S_3), cementing cassiterite (not confirmed by Ramdohr).

The veins and telluride minerals of Kalgoorlie are described in detail by F. L. Stilwell; [26] H. Borchert [27] gives etching lists for tellurides; L. Tokody [28] has analysed hessite; G. Vavrinecz [29] describes antimony-rich enargite, from Hungary. *X*-Ray methods have been used by F. A. Bannister and M. H. Hey[30] to determine the minerals of S. African platinum concentrates, and for the distinction of pyrite from marcasite,[31] the latter result confirming the earlier work of Allen and others. Bushveld nickel veins are discussed by R. D. Hoffman.[32]

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[11] *J. Inst. Petrol. Tech.*, 1931, **17**, 338; *A.*, 1931, 931.

[12] *Ibid.*, p. 334; *A.*, 1931, 931.

[13] *Ibid.*, p. 331.

[14] F. W. Freise, *Chem. Erde*, 1932, **7**, 24; *A.*, 596.

[15] *Centr. Min.*, 1932, 356.

[16] *Amer. J. Sci.*, 1931, [v], **22**, 215; *A.*, 1931, 1146.

[17] *Ann. Chim.*, 1932, [x], **18**, 5.

[18] *Kali, Russia*, 1932, No. 2, 25.

[19] *Tsch. min. petr. Mitt.*, 1931, **41**, 197.

[20] F. L. Stilwell, *Proc. Austral. Inst. Min. Met.*, 1931, 1; *A.*, 1931, 1029.

[21] S. Piña de Rubies, *Anal. Fis. Quím.*, 1931, **29**, 699; *A.*, 248.

[22] H. C. Gunning, *Econ. Geol.*, 1931, **26**, 215.

[23] *Ibid.*, p. 453.

[24] *Ibid.*, p. 241.

[25] *Centr. Min.*, 1932, 354.

[26] *W. Austral. Geol. Surv. Bull.* 94, 1929; *A.*, 495.

[27] *Jahrb. Min.*, 1930, [*A*], **61**, 101.

[28] *Z. Krist.*, 1932, **82**, 154; *A.*, 595.

[29] *Bán. Kohás. Lapok*, 1931, **64**, 438; *Chem. Zentr.*, 1932, i, 931.

"Unmixing" has been studied for covellite–chalcocite by A. M. Bateman and S. G. Lasky;[33] for chalcopyrite–blende and cubanite by E. Clar;[34] and for chalcopyrite–cubanite–pyrrhotite by W. H. Newhouse.[35] General descriptions of the corresponding microstructures have been given, especially by G. M. Schwartz.[36] Several detailed accounts have been given of N. Rhodesian copper deposits,[37] which are usually regarded as impregnations from the neighbouring granite.

Sulvanite, Cu_3VS_4,[38] has been found in Utah. L. W. Staples and C. W. Cook[39] describe the molybdenite veins of Climax, Col.

Oxides.—O. Mügge[40] describes a method for determining the temperature of formation of quartz by heating at 600°. Amethyst mines in Brazil are described by R. Brauns;[41] according to J. Hoffmann,[42] amethyst colours can be imitated by exposing silicate glasses to radium rays. Colour in spinel is shown by K. Schlossmacher[43] to be due to 1—4% of Fe (Co, Mn, Cr absent); intermediate colours are due to reduction.

Galaxite, a new spinel, MnO,Al_2O_3, is described by C. S. Ross and P. F. Kerr[44] with alleghanyite ($5MnO,2SiO_2$). M. Donath[45] finds 2·42% ZnO in chromite from Ramberget; chromite from Togoland has been analysed by N. Kouriatchy.[46] H. H. Read[47] has described the formation of corundum–spinel xenoliths from Aberdeenshire.

Water-soluble humus plays a great part in the formation of lake iron ores; O. Aschan[48] has analysed the organic matter in Finnish lake waters. S. Goldsztaub[49] describes the formation of parallel growths of hæmatite on dehydrating natural ferric hydroxides;

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[30] *Min. Mag.*, 1932, **23**, 188; *A.*, 1014.

[31] *Ibid.*, p. 179.

[32] *Econ. Geol.*, 1931, **26**, 202.

[33] *Ibid.*, 1932, **27**, 52.

[34] *Centr. Min.*, 1931, 147.

[35] *Amer. Min.*, 1931, **16**, 334.

[36] *Econ. Geol.*, 1931, **26**, 739.

[37] See *Econ. Geol.*, 1931—1932.

[38] *Amer. Min.*, 1931, **16**, 557.

[39] *Ibid.*, p. 1.

[40] *Z. Krist.*, 1932, **82**, 451; *A.*, 829.

[41] *Centr. Min.*, 1932, 97.

[42] *Z. anorg. Chem.*, 1931, **196**, 225; *A.*, 1931, 579.

[43] *Z. Krist.*, 1931, **76**, 370, 377; *A.*, 1931, 459, 545.

[44] *Amer. Min.*, 1932, **17**, 1; *A.*, 1228.

[45] *Ibid.*, 1931, **16**, 484; *A.*, 1107.

[46] *Compt. rend.*, 1931, **192**, 1669; *A.*, 1931, 1029.

[47] *Geol. Mag.*, 1931, **68**, 446.

[48] *Arkiv Kemi, Min. Geol.*, 1932, **10**, No. 14, 1; *A.*, 716.

[49] *Compt. rend.*, 1931, **193**, 533; *A.*, 1931, 1390.

the stability relations of these minerals have been discussed by G. Tunell and E. Posnjak[50] with reference to the theoretical conclusions of J. W. Gruner. Further descriptions of the important Wabana iron ore have been given by A. O. Hayes.[51] Perhaps the greatest iron ore masses in the world are the Brazilian itabirites, which occur as stratified pure red hæmatite and as micaceous schist.[52] The peculiar banding of the L. Superior iron formation is attributed by R. J. Hartman and R. M. Dickey[53] to Liesegang effects; secondary ores are described by C. K. Leith.[53a]

W. J. O'Leary and J. Papish[54] find up to 0·25% Cr in ruby. A. Achenbach[55] finds that artificial gibbsite passes into boehmite about 200° and dehydrates further at 350°. W. Büssem and F. Köberich[56] describe the dehydration of brucite to periclase in parallel orientation. Analyses are given for pyroaurite[57] and hydromagnesite.[58] Microscopical studies of the manganese oxides have been made by S. R. B. Cooke, W. Howes, and A. Emery,[59] also by J. Orcel and S. Pavlovitch.[60] G. Natta and M. Baccaredda[61] find both Sb_2O_4 and Sb_2O_5, with calcium, in various antimony ochres. C. Zapffe has studied deposition of manganese from water supplies, sometimes by bacteria.[61a]

Carbonates.—Bacterial precipitation of lime is described by H. Fischer, W. Bavendamm, P. Kalantarian and A. Petrossian,[62] who find a new bacterium, *B. Sewanense*. *X*-Ray investigations by F. K. Mayer[63] show the presence of vaterite, changing to aragonite and calcite, in the shells of fresh-water snails. H. Wattenberg[64] has suggested that liquid carbon dioxide could be formed under the pressures that obtain in ocean depths. Conditions for the precipitation of dolomite have been discussed by O. Bär[65] and H.

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[50] *Econ. Geol.*, 1931, **26**, 337, 442, 783, 894; **27**, 189; *A.*, 1931, 800.

[51] *Ibid.*, 1931, **26**, 1.

[52] E. A. Scheibe, *Arch. Eisenhüttenw.*, 1931—1932, **5**, 391; *A.*, 492.

[53] *J. Physical Chem.*, 1932, **36**, 1129; *A.*, 492.

[53a] *Econ. Geol.*, 1931, **26**, 274.

[54] *Amer. Min.*, 1931, **16**, 34; *A.*, 1931, 455.

[55] *Chem. Erde*, 1931, **6**, 307; *A.*, 1931, 1029.

[56] *Z. physikal. Chem.*, 1932, [*B*], **17**, 310.

[57] E. Aminoff and R. Broomé, *K. Svenska Vetenskaps Akad. Handl.*, 1931, [iii], **9**, No. 5, 4; *A.*, 1931, 1029.

[58] G. R. Levi and D. Ghiron, *Gazzetta*, 1932, **62**, 218; *A.*, 595.

[59] *Amer. Min.*, 1931, **16**, 209.

[60] *Bull. Soc. franç. Min.*, 1931, **54**, 108; *A.*, 1106.

[61] *Atti R. Accad. Lincei*, 1932, [vi], **15**, 389; *A.*, 829.

[61a] *Econ. Geol.*, 1931, **26**, 799.

[62] *Zentr. Bakt. Par.*, 1932, **85**, 431.

[63] *Chem. Erde*, 1931, **6**, 239; *A.*, 1931, 596.

[64] *Nature*, 1932, **130**, 26; *A.*, 829.

[65] *Centr. Min.*, 1932, [*A*], 46; *A.*, 1106.

Udluft.[66] E. Köhler[67] finds that schaumspat is a pseudomorph of dolomite after gypsum. J. Klärding[68] has studied the roasting of ferrous carbonate, with formation of Fe_3O_4. Rocks consisting of dolomite, with zones of transition to magnesite and to siderite, occur in the S. Urals.[69] Hydrated cupric carbonates, with malachite, have been prepared by V. Auger and Mme. Poulenc-Ferrand.[70] A curious observation has been made by F. Stöber,[71] who finds that on imitating the formation of Fontainebleau calcites by growing sodium nitrate in sand, the rate of growth is very greatly increased in the presence of the sand. F. Taboury[72] has found efflorescence of calcium acetate upon calcite specimens that had been stored in oak cases, due to acid from the wood.

Silicates.—G. W. Ward[73] has carried out a very thorough investigation of the black tourmalines; optical properties are given, with several new analyses. While accepting the ordinary chemical replacements, he concludes that it would be futile to propose new molecules; a simple formula cannot be found. F. Machatschki[74] proposes for tourmaline the (physical) formula $XY_9B_3Si_6H_xO_3$ where X = (Cu, Na), Y = (Li, Mg, Mn, Fe, Al); NaSi is replaceable by CaAl, and SiMg by AlAl.

"Green-earth" in the Tyrol occurs between volcanic rocks and limestone; it is compared by K. Hummel[75] with glauconite, and its formation is attributed to halmyrolysis, *i.e.*, submarine alteration, of igneous rock. Parase–piolite has been found by H. Meixner[76] in the Styrian magnesite deposits. *Ashtonite*[77] and *clinoptilolite*[78] are new aluminosilicates related to ptilolite. Zunyite from Guatemala has been analysed by C. Palache.[79] G. Liberi[80] deduces the formula $4BeO,Al_2O_3,7SiO_2$ for beryl from Erythræa; danburite has been described by Z. Harada.[81]

E. S. Larsen and W. T. Schaller[82] describe serendibite from a limestone–granite contact. Dumortierite from India has been analysed by S. K. Chatterjee.[83]

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[66] *Z. deut. geol. Ges.*, 1931, **83**, 1; *A.*, 1931, 1391.

[67] *Chem. Erde*, 1931, **6**, 257; *A.*, 1931, 596.

[68] *Z. anorg. Chem.*, 1932, **207**, 246.

[69] L. M. Miropolski, *Bull. Acad. Sci. U.R.S.S.*, 1932, 829; *A.*, 1015.

[70] *Compt. rend.*, 1932, **194**, 788; *A.*, 481.

[71] *Chem. Erde*, 1931, **6**, 357; *A.*, 1931, 1030.

[72] *Bull. Soc. chim.*, 1931, [iv], **49**, 1289; *A.*, 39.

[73] *Amer. Min.*, 1931, **16**, 145; *A.*, 38.

[74] *Z. Krist.*, 1929, **70**, 211; **71**, 45; *A.*, 1931, 595.

[75] *Chem. Erde*, 1931, **6**, 468; *A.*, 140.

[76] *Tsch. min. petr. Mitt.*, 1932, **43**, 182; *A.*, 1107.

[77] E. Poitevin, *Amer. Min.*, 1932, **17**, 105.

[78] W. T. Schaller, *ibid.*, p. 128; *A.*, 1228.

[79] *Ibid.*, p. 304.

[80] *Ann. Chim. Appl.*, 1932, **22**, 544; *A.*, 1106.

[81] *Z. Krist.*, 1931, **79**, 349; *A.*, 1931, 1266.

[82] *Amer. Min.*, 1932, **17**, 457; *A.*, 1228.

The hauyne group is particularly complex: T. F. W. Barth[84] suggests physical formulæ, and L. H. Borgström[85] proposes the substitution Ca,Na. D. S. Beliankin renames a sulphate–cancrinite *wischnewite*.[86] Helvite has been analysed by H. Bowley.[87] Sodalites have been analysed by K. Haraguchi[88] and by W. Brendler.[89] It is sometimes difficult to distinguish nepheline from sodalite; a method with *X*-rays, applicable to thin sections, has been developed by F. A. Bannister,[90] with several analyses by M. H. Hey; similar methods are given for analcime and leucite.[91] The scapolite group has been reviewed by L. H. Borgström,[92] who regards them as isomorphous mixtures of type $(NaAlSi_3O_8)_3$, in which albite may be replaced by anorthite, and NaCl by $CaCO_3$, $CaSO_4$, $\frac{1}{2}Na_2CO_3$, $\frac{1}{2}Na_2SO_4$, Ca atoms replacing Na. F. Zambonini and V. Caglioti[93] discuss new analyses of sarcolite.

Among the hydrated silicates, H. Hueber and W. Freh[94] find that "kupferpecherz" is a limonitic chrysocolla, isotropic. A. Schoep[95] concludes that plancheite from Katanga is variable and in part identical with shattuckite, in part with bisbeeite from Arizona; katangite is chrysocolla. Willemite prepared by A. Karl[96] is fluorescent like the natural mineral. *Bultfonteinite*, $2Ca(OH,F)_2,SiO_2$, a new mineral from Kimberley diamond mines, is described by J. Parry, A. F. Williams, and F. E. Wright.[97] S. Iimori, T. Yoshimura, and S. Hata[98] describe *nagatelite*, a new pegmatite mineral resembling allanite. *Sanbornite*[99] has the composition $BaSi_2O_5$. Analyses have been made of lessingite,[1] serandite, spadaite,[2] joaquinite, gadolinite, pumpellyite, bavenite.[3] G. W. Bain has discussed the formation of chrysotile veins.[3a]

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[83] *Rec. Geol. Surv. India*, 1931, **65**, 285; *A.*, 247.

[84] *Amer. Min.*, 1932, **17**, 466.

[85] *Z. Krist.*, 1931, **76**, 481; *A.*, 140.

[86] *Centr. Min.*, 1931, 190; *A.*, 249.

[87] *J. Roy. Soc. W. Australia*, 1932, **18**, 83.

[88] *Chikyu*, 1928, **10**, 262.

[89] *Centr. Min.*, 1932, [*A*], 42; *A.*, 1106.

[90] *Min. Mag.*, 1931, **22**, 569; *A.*, 1931, 1390.

[91] *Ibid.*, p. 469; *A.*, 1931, 595.

[92] *Z. Krist.*, 1931, **76**, 481.

[93] *Compt. rend.*, 1931, **192**, 967; *A.*, 1931, 706.

[94] *Centr. Min.*, 1931, 296.

[95] *Bull. Soc. franç. Min.*, 1930, **53**, 375.

[96] *Compt. rend.*, 1932, **194**, 1743; *A.*, 715.

[97] *Min. Mag.*, 1932, **23**, 145; *A.*, 1015.

[98] *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1930, **15**, 83; *A.*, 1931, 459.

[99] A. F. Rogers, *Amer. Min.*, 1932, **17**, 161; *A.*, 1228.

[1] *Trans. Inst. Econ. Min. Met., Moscow*, 1930, Nos. 44, 46.

[2] *Amer. Min.*, 1931, **16**, pp. 344 and 231 resp.

[3] *Ibid.*, 1932, **17**, pp. 308, 97, 338, 409 resp.; *A.*, 1228.

[3a] *Econ. Geol.*, 1932, **27**, 39.

Pyroxenes.—N. Sundius[4] has given a very full account of the triclinic (Fe, Mn, Ca) pyroxenes. Like the carbonates, they form a series of incompletely miscible crystals, the intermediate members being sobralite (Fe, Mn), bustamite (Mn, Ca), and hedenbergite $(Fe,Ca)SiO_3$. Bustamite does not form a complete series of solutions with rhodonite, and the optical properties are not continuous: it is suggested that bustamite is a ferriferous wollastonite; a wide gap between bustamite and wollastonite is attributed to the formation of pseudo-wollastonite at higher temperatures. *X*-Ray data for enstatite are given by B. Gossner and F. Mussgnug;[5] F. Rodolico[6] gives analyses of diopside and tremolite from Italy. A pyroxene from S. Africa[7] contains 1·96% Cr_2O_3. T. F. W. Barth[8] records a titaniferous augite (TiO_2, 3·75%), and has discussed the occurrence of pyroxenes in basalt;[9] this subject has been further examined by S. Tsuboi.[9a]

Amphiboles.—Since the general acceptance of amphibole formulæ with (F, OH) as an essential constituent, the whole question of the stability relations of these minerals has come under review. The formulation is further discussed by W. Kunitz[10] and by E. Posnjak and N. L. Bowen,[10a] who agree with the tremolite formula of Schaller and Warren; the water is lost at about 900°, when the crystal changes to pyroxene and cristobalite; a mineral obtained from the dry melt proves not to be an amphibole.[11] A. N. Winchell[12] also has discussed the application of Warren's formula to many analyses, with plots of the optical data. V. E. Barnes[13] shows that green hornblende is converted into the "basaltic" variety by heating in air; iron is essential to the change; in hydrogen, green hornblende is re-formed. Analyses of both varieties are given by T. Ichimura.[14] Formulæ for the alkali amphiboles have been proposed by H. Berman and E. S. Larsen,[15] who deduce a limited miscibility. Lattice dimensions for the monoclinic amphiboles have been determined by G. Greenwood and A. L. Parsons,[16] and analyses have been given for tremolite by A. L. Coulson,[17] for babingtonite by C. Palache and F. A. Gonyer,[18] for hornblende by H. Heritsch,[19] and for manganese-rich ferroanthophyllite by A. Orlov.[20] Grunerite from Pierrefitte is described by H. V. Warren,[21] and N. Sundius [22] has discussed various grunerites, with analyses and optical properties, with respect to their manganese content. Veins of nephrite after pyroxene are described by H. Rose and J. Fromme,[23] and specimens of various "jade" minerals (previously identified mineralogically) have been tested by *X*-ray methods by P. L. Merritt.[24]

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[4] *Amer. Min.*, 1931, **16**, 411, 488; *A.*, 1228.

[5] *Z. Krist.*, 1929, **70**, 234; *A.*, 1931, 595.

[6] *Atti R. Accad. Lincei*, 1931, [vi], **13**, 705; *A.*, 1931, 1391.

[7] H. O'Daniel, *Z. Krist.*, 1930, **75**, 575; *A.*, 1931, 594.

[8] *Jahrb. Min., Beil.-Bd.*, 1931, [*A*], **64**, 217; *A.*, 494.

[9] *Amer. Min.*, 1931, **16**, 195; *A.*, 494.

[9a] *Jap. J. Geol. Geog.*, 1932, **10**, 67.

[10] *Jahrb. Min., Beil.-Bd.*, 1930, [*A*], **60**, 171; *A.*, 1931, 595.

[10a] *Amer. J. Sci.*, 1931, [v], **22**, 203; *A.*, 1931, 446. [11] *Ibid.*, p. 193.

[12] *Amer. Min.*, 1931, **16**, 250.

[13] *Ibid.*, 1930, **15**, 393; *A.*, 1931, 818.

[14] *Min. Mag.*, 1931, **22**, 561; *A.*, 1931, 1390.

[15] *Amer. Min.*, 1931, **16**, 140; *A.*, 38.

[16] *Univ. Toronto Stud. Geol.*, 1931, No. 30, 29; *A.*, 493.

Micas, etc.—Fuchsite with 2·74% Cr_2O_3 has been analysed by S. K. Chatterjee; [25] H. Meixner [26] has tested the various methods for determining chromium in mica, and finds earlier methods were not reliable. A very important source of error in micas may be the omission to separate the rarer alkali metals; F. L. Hess and J. J. Fahey [27] have found 3·14% of cæsium oxide in a biotite. J. Jakob [28] continues his studies with several analyses of biotites and phlogopite; he considers that Ti never replaces Al or Si, but always 2Mg; apparently lime is again completely absent from these micas. F. C. Phillips [29] describes a margarite in which much of the lime has been replaced by soda. Chlorites have been analysed by A. Goossens,[30] S. Pavlovitch [31] (from corundum rocks), and S. Kozik [32] (from Tatra granite); also by G. L. Dschang,[33] who interprets 8 new analyses as mixtures of serpentine, amesite, etc. J. Orcel [34] found for ripidolite heated in nitrogen a sharp maximum at 780° due to $2FeO + H_2O = Fe_2O_3 + H_2$. Chamosite, the chlorite of the iron ores, was early obtained from Schmiedefeld; the present generally accepted formula rests upon analyses of better material; H. Jung [35] has separated chamosite from this ore and obtains the formula $5Al_2O_3,15RO,11SiO_2,16H_2O$, the accepted ratios being 5 : 15 : 10.

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[17] *Rec. Geol. Surv. India*, 1931, **63**, 444; *A.*, 1931, 595.

[18] *Amer. Min.*, 1932, **17**, 295.

[19] *Centr. Min.*, 1931, 364.

[20] *Ibid.*, 1932, 269.

[21] *Min. Mag.*, 1931, **22**, 477; *A.*, 1931, 595.

[22] *Amer. J. Sci.*, 1931, [v], **21**, 330; *A.*, 1228.

[23] *Centr. Min.*, 1932, 301.

[24] *Amer. Min.*, 1932, **17**, 497.

[25] *Rec. Geol. Surv. India*, 1932, **65**, 536; *A.*, 1107.

[26] *Centr. Min.*, 1931, 318.

[27] *Amer. Min.*, 1932, **17**, 173; *A.*, 1228.

[28] *Z. Krist.*, 1932, **82**, 271; *A.*, 715.

[29] *Min. Mag.*, 1931, **22**, 482; *A.*, 1931, 595.

[30] *Natuurwetensch. Tijds.*, 1931, **13**, 119; *A.*, 1931, 817.

[31] *Bull. Soc. franç. Min.*, 1930, **53**, 535.

[32] *Bull. Acad. Polonaise*, 1930, [*A.*], 536; *A.*, 1931, 706.

[33] *Chem. Erde*, 1931, **6**, 416; *A.*, 1931, 1030.

[34] *Bull. Soc. franç. Min.*, 1930, **52**, 194; *A.*, 1931, 594.

[35] *Chem. Erde*, 1931, **6**, 275; *A.*, 1931, 1030.

X-Ray patterns distinguish it from thuringite. J. P. Arend[36] gives analyses of ooliths and gangue in the Lorraine ores.

Felspars.—Methods for the identification of the felspars are described in detail by K. Chudoba, " Felspäte u. ihre prakt. Bestimmung " (Stuttgart, 1932), and H. Ebert[37] discusses the determination of acid plagioclases. Anorthoclase from an Icelandic lava is described by L. Hawkes and H. F. Harwood;[38] the surrounding glass must have undergone a subsequent change in composition with increase in sodium oxide. Certain felspars apparently deviate from the standard formula; D. S. Beliankin,[39] who has collected preliminary data, fails to confirm Jakob's negative results for CaO and BaO. A. G. MacGregor[40] uses cloudiness in the felspars as a criterion for thermal metamorphism.

Clays.—Kaolin has been synthesised by W. Noll[41] by heating the precipitate in a pressure bomb at 300°. H. Jung[42] shows that kaolin can be partly dehydrated reversibly, yielding an amorphous product up to 550°; the heat of hydration in this reaction has been determined by E. Klever and E. Kordes.[43] Kaolin in shales is attributed by J. Kuhl[44] to the action of sulphuric acid. Japanese acid clays have been further studied by several workers: the *X*-ray patterns resemble those of fuller's earth, attributed to a common crystalline clay-mineral; thermal dehydration shows rapid loss at 70—260° and at 450—700°; basic and acid dyes are adsorbed, especially after removal of acid-soluble aluminium and iron. P. F. Kerr[45] discusses the presence of montmorillonite. General discussions on clay are given by F. Kästner and F. K. Mayer, C. E. Marshall, F. H. Norton and F. B. Hodgdon, and R. Bradfield.[46] Vanadium occurs in red clay from Devonshire,[47] while the associated nodules contain as much as 13·96% of V_2O_5.

Zeolites.—M. H. Hey[48] gives a general review of the literature on zeolites; 16 thomsonites analysed by him[49] show both replacements CaAl–NaSi and Ca–Na_2. Dehydration of heulandite is described by P. Gaubert,[50] and P. G. Bird [51] has shown that zeolites can be dehydrated by freezing. Base exchange is used by G. Austerweil [52] as a means of purifying salt preparations; when the exchange results in an insoluble compound the whole of a salt such as Na_2CrO_4 may be removed (by a zeolite containing lead). Base exchange in permutite has been extensively studied by E. Gruner [53] and others.

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[36] *Compt. rend.*, 1932, **194**, 736, 990; *A.*, 360, 493, 595.

[37] *Tsch. min. petr. Mitt.*, 1931, **42**, 8; *A.*, 1931, 1390.

[38] *Min. Mag.*, 1932, **23**, 163; *A.*, 1015.

[39] *Centr. Min.*, 1931, 356.

[40] *Min. Mag.*, 1931, **22**, 524; *A.*, 1931, 1029.

[41] *Naturwiss.*, 1932, **20**, 366; *A.*, 716.

[42] *Chem. Erde*, 1932, **7**, 113; *A.*, 596.

[43] *Veröff. Kaiser Wilhelm-Inst. Silikatforsch.*, 1930, **3**, 17.

[44] *Bull. Acad. Polonaise*, 1931, [*A*], 665.

[45] *Amer. Min.*, 1932, **17**, 192; *Econ. Geol.*, 1931, **26**, 153; *A.*, 1228.

[46] See *Abstracts* under these names.

[47] G. E. L. Carter, *Min. Mag.*, 1931, **22**, 609; *A.*, 1931, 1390.

[48] *Ibid.*, 1930, **22**, 422.

[49] *Ibid.*, 1932, **23**, 51; *A.*, 715.

Phosphates.—The apatite minerals have a peculiarly varied composition: S. B. Hendricks, M. E. Jefferson, and K. M. Mosley [54] have analysed a variety of products, partly synthetic, and conclude that F in fluorapatite can be replaced by CO_3, OH, SO_4, SiO_4, O, Cl, Br, or I, yielding minerals such as voelkerite, staffelite, collophanite, etc. *X*-Ray photographs show that animal bone is a carbonate apatite, which gains fluorine on fossilisation. Turquoise analyses have been discussed by H. Jung.[55]

J. Lietz [56] has compared the constants for various analysed minerals in the pyromorphite group; the order is pyromorphite–mimetite–vanadinite. A Spanish vanadinite is described by F. M. Martin.[57] Intensely blue wavellite [58] contains 0·5% Cr_2O_3. Veszelyite from Moravia [59] apparently forms an isomorphous series with arakawite and kipushite; new crystals of the latter have been determined by H. Buttgenbach.[60] *Leucophosphite* is a new hydrous phosphate of K, Fe, Al.[61]

E. Dittler and H. Hueber [62] have analysed mottramite from Bolivia, for which they obtain a general formula that also agrees with the Otavi descloizite. Psittacinite [63] has the composition $2PbO,2CuO,V_2O_5,2H_2O$. Fervanite [64] is $2Fe_2O_3,2V_2O_5,5H_2O$.

Arsenoklasite is a new manganese arsenate from Långban.[65] *Legrandite*, a complex zinc arsenate, is described by J. Drugman, M. H. Hey, and F. A. Bannister.[66] T. L. Walker [67] gives analyses of triphylite with columbite, from a pegmatite in Manitoba.

[50] *Bull. Soc. franç. Min.*, 1930, **52**, 162. [51] *Ind. Eng. Chem.*, 1932, **24**, 793.

[52] *Compt. rend.*, 1931, **193**, 1013. [53] *Z. anorg. Chem.*, 1932, **204**, 321, etc.

[54] *Z. Krist.*, 1932, **81**, 352; *A.*, 494. [55] *Chem. Erde*, 1932, **7**, 77; *A.*, 596.

[56] *Z. Krist.*, 1931, **77**, 437; *A.*, 1931, 817.

[57] *Anal. Fis. Quim.*, 1932, **30**, 377; *A.*, 830.

[58] A. Orlov, *Z. Krist.*, 1931, **77**, 317; *A.*, 1931, 707.

[59] V. Zsivny, *ibid.*, 1932, **82**, 87; *A.*, 595.

[60] *Bull. Acad. roy. Belg.*, 1931, [v], **18**, 43; *A.*, 494.

[61] E. S. Simpson, *J. Roy. Soc. W. Australia*, 1931–1932, **18**, 69.

[62] *Tsch. min. petr. Mitt.*, 1931, **41**, 173; *A.*, 1931, 707.

[63] S. Taber and W. T. Schaller, *Amer. Min.*, 1930, **15**, 575; *A.*, 1931, 817.

[64] F. L. Hess and E. P. Henderson, *ibid.*, 1931, **16**, 273; *A.*, 38.

[65] G. Aminoff, *K. Svenska Vetenskaps Akad. Handl.*, 1931, [iii], **9**, No. 5, 52; *A.*, 1931, 1028.

[66] *Min. Mag.*, 1932, **23**, 175; *A.*, 1015.

[67] *Univ. Toronto Stud. Geol.*, 1931, No. 30, 9; *A.*, 493.

Sulphates, etc.—M. H. Hey[68] finds that pink specimens of fauserite from Hungary are really epsomite, stained with cobalt; cupriferous melanterite[69] occurred in an ancient stope in Cyprus. Natural ferrous sulphates are discussed by R. Scharizer,[70] and artificial voltaites by B. Gossner and E. Fell.[71] Pickeringite, a hydrous sulphate of aluminium and magnesium, is described by R. L. Rutherford.[72] Other analyses include krausite and creedite;[73] castanite from California[74] and from Chuquicamata;[75] roeblingite from Franklin Furnace;[76] pickeringite.[77] C. Kuzniar[78] describes secondary deposits of Glauber's salt in potash-bearing sediments.

New minerals include *Letovicite*, $(NH_4)_3H(SO_4)_2$,[79] in coal-mine dumps; *Schairerite*, $Na_2SO_4,Na(F,Cl)$;[80] *Ardealite*, $CaHPO_4,CaSO_4,4H_2O$;[81] *Klebelsbergite*, a basic antimony sulphate;[82] *Glaucocerinite*, basic sulphate of Zn, Cu, Al;[83] "*Alkanasul*," sulphate of Al and alkalis.[84]

Cuprotungstite has been analysed by W. T. Schaller.[85] Details of the recently discovered pitchblende-silver deposit at Gt. Bear Lake in Canada are given by D. F. Kidd.[86] Manganese compounds include bixbyite,[87] coronadite[88] and romanechite;[89] the new mineral *magnesiosussexite*, $2(Mg,Mn)O,B_2O_3,H_2O$, isomorphous with camsellite, occurs in veinlets in the Michigan hæmatite.[90]

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[68] *Min. Mag.*, 1931, **22**, 510; *A.*, 1931, 1029.

[69] *Ibid.*, 1930, **22**, 413; *A.*, 1931, 191.

[70] *Z. Krist.*, 1930, **75**, 67; *A.*, 1931, 459.

[71] *Ber.*, 1932, **65**, [*B*], 393.

[72] *Amer. Min.*, 1932, **17**, 401.

[73] W. F. Foshag, *ibid.*, 1931, **16**, 352; 1932, **17**, 75; *A.*, 139.

[74] A. F. Rogers, *ibid.*, 1931, **16**, 396; *A.*, 140.

[75] M. C. Bandy, *ibid.*, 1932, **17**, 534.

[76] R. Blix, *ibid.*, 1931, **16**, 455; *A.*, 1107.

[77] R. L. Rutherford, *ibid.*, 1932, **17**, 401.

[78] *Bull. Acad. Polonaise*, 1931, [*A*], 411; *A.*, 714.

[79] J. Sekanina, *Z. Krist.*, 1932, **83**, 177; *A.*, 1015.

[80] W. F. Foshag, *Amer. Min.*, 1931, **16**, 133.

[81] J. Schadler, *ibid.*, 1932, **17**, 251.

[82] V. Zsivny, *Math. Nat. Anz. Ungar. Akad. Wiss.*, 1929, **46**, 19; *Chem. Zentr.*, 1930, ii, 3530.

[83] E. Dittler and R. Koechlin, *Centr. Min.*, 1932, 13.

[84] J. Westman, *Bol. Min. Soc. nac. Min.*, 1931, **43**, 433; *Chem. Zentr.*, 1932, i, 573.

[85] *Amer. Min.*, 1932, **17**, 234; *A.*, 1228.

[86] *Econ. Geol.*, 1932, **27**, 145.

[87] H. Corti, *Anal. Asoc. Quim. Argentina*, 1931, **19**, 109; *A.*, 140.

[88] J. Orcel, *Compt. rend.*, 1932, **194**, 1956; *A.*, 716.

[89] F. Zambonini and V. Caglioti, *ibid.*, 1931, **192**, 750; *A.*, 1931, 707.

[90] J. W. Gruner, *Amer. Min.*, 1932, **17**, 509.

Water, etc.

K. Higashi, K. Nakamura, and R. Hara[91] have determined the specific gravity and vapour pressure of sea-water at various concentrations between 0° and 175°. Copper is found by electrolysis to be about 10 mg. per cu.m.;[92] ammonia in sea-water varies between 0 and 48 mg. per cu.m. at the surface, up to 350 mg. at 25 m. depth.[93] R. Willstätter[94] attributes the blue colour to copper ammines. Hydrogen-ion studies have been made by D. Goulston[95] and T. G. Thompson and R. U. Bonnar.[96] Off Brest the reducing power for potassium permanganate is found by P. Chauchard[97] to rise somewhat in stormy weather; below 100 m. depth it rapidly diminishes. The silica content is discussed by H. M. King,[98] and N. W. Rakestraw[99] has determined phosphate, nitrate, and nitrite contents near Cape Cod.

Formaldehyde in rain water is attributed by N. R. Dhar and A. Ram[1] to direct formation in ultra-violet light. C. Srikantia[2] gives the combined nitrogen in rain water at Bangalore. Rain analyses at Geneva, N.Y., for a 10-year period have been recorded by R. C. Collison and J. E. Mensching.[3] Waters from 80 Japanese lakes have been analysed by S. Yoshimura.[4] A. H. Wiebe[5] has discussed the bearing of dissolved phosphorus and nitrogen in the Mississippi upon the plankton. The relation of iodine contents to goitre has been further investigated by J. Kupzis;[6] adequacy of iodine supply can be ascertained from the amount excreted. The distribution of iodine in water and coal is described by R. Wache;[7] iodine is without effect as a fertiliser, but is assimilated. E. Schantl[8] records 0·015% of magnesium iodide in well waters from the E. Indies. Many spring waters have been analysed. Picon[9] has investigated the organic carbon content, which is not directly related to the results with potassium permanganate. Electrical conductivity tests are discussed by P. S. Tutundžić,[10] and by E. Bovalini and E. Vallesi,[11] who find the method useful within certain limits as a guide to the dissolved matter. Muds have been studied by D. M. Reid,[12] H. B. Moore,[13] and others, with reference to p_H and content of phosphate, oxygen, etc. Work on natural gases includes several discussions of the hydrocarbon contents; krypton and xenon are estimated by N. P. Pentchev [14] in several Bulgarian gases.

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[91] *J. Soc. Chem. Ind. Japan*, 1931, **34**, 72B; *A.*, 1931, 1265.

[92] W. R. G. Atkins, *J. Marine Biol. Assoc.*, 1932, **18**, 193; *A.*, 714.

[93] H. R. Seiwell, *Ecology*, 1931, **12**, 485; *A.*, 1931, 1145.

[94] *Naturwiss.*, 1930, **18**, 868.

[95] *J. Proc. Roy. Soc. N.S.W.*, 1931, **65**, 43; *A.*, 247.

[96] *Ind. Eng. Chem. (Anal.)*, 1931, **3**, 393; *A.*, 1931, 1389.

[97] *Compt. rend.*, 1932, **194**, 1256; *A.*, 594.

[98] *Contr. Canadian Biol. Fish.*, 1931, **7**, Nos. 8–11, D, Nos. 1–4, 129–137.

Science, 1932, **75**, 417; *A.*, 594. [1] *Nature*, 1932, **130**, 313; *A.*, 1106.

Mysore Univ. J., 1930, **4**, 195; *A.*, 1931, 594.

New York State Agric. Exp. Sta. Tech. Bull., 1932, No. 193; *A.*, 829.

Proc. Imp. Acad. Tokyo, 1932, **8**, 94; *A.*, 594.

Science, 1931, **73**, 652; *A.*, 1931, 930.

Latvij. Univ. Raksti, 1930, **1**, 425; *A.*, 1931, 331.

[7] *Mitt. Lab. preuss. geolog. Landesanst.*, 1931, No. 13, 43; *Chem. Zentr.*, 1931, ii, 981.

[8] *Chem.-Ztg.*, 1932, **56**, 341; *A.*, 594.

[9] *Compt. rend.*, 1932, **194**, 1175; *A.*, 594.

Soils.

H. Keller [15] describes methods of soil charting in U.S.A. Soil colours have been classified by N. A. Archangelskaya,[16] using Ostwald's colour disc. There are numerous papers describing soil varieties, which it is only possible to summarise in brief. Special soils result from the weathering of volcanic tuffs, loess and laterite; in other cases vegetable decay products are dominant, forming peaty, pine, and other special types. Several soil surveys are recorded from Australia, the Nile, and Eastern Europe.

Coal.

A. Duparque [17] considers that most coking coals are produced from lignin, bituminous coals from cutin; anthracites belonging to the latter class differ from the others. R. Lieske and K. Winzer [18] also support the lignin theory, and G. Stadnikow [19] finds well-preserved lignin in shale. On the other hand, P. Krassa [20] finds that in fungal decomposition of wood, lignin is destroyed. The action of bacteria on cellulose is discussed by F. Fischer [21] and S. A. Waksman,[22] while specific organisms in coal are described by R. Lieske.[23] Base exchange involving the roof-clay has been suggested as affecting the seams, but this is discounted by W. H. A. Penseler.[24]

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[10] *Bull. Soc. chim. Yougoslav.*, 1931, **2**, 77; 1932, **3**, 33; *A.*, 829.

[11] *Ann. Chim. Appl.*, 1931, **21**, 51; *A.*, 1931, 458.

[12] *J. Marine Biol. Assoc.*, 1932, **18**, 299; *A.*, 714.

[13] *Ibid.*, 1931, **17**, 325; *A.*, 1931, 930.

[14] *Compt. rend.*, 1931, **192**, 691; *A.*, 1931, 594.

[15] *Z. Pflanz. Düng.*, 1932, **24**, *A.*, 38.

[16] *Trans. Dokuchaiev Soil Inst.*, 1932, **6**, 197; *A.*, 1108.

[17] *Compt. rend.*, 1931, **192**, 1472, 1257.

[18] *Brennstoff-Chem.*, 1931, **12**, 205; *A.*, 1931, 931.

[19] *Ibid.*, 1932, **13**, 247; *A.*, 1015.

[20] *Angew. Chem.*, 1932, **45**, 21; *A.*, 360.

[21] *Proc. III Int. Conf. Bit. Coal*, 1932, **2**, 809; *A.*, 1107.

[22] *Brennstoff-Chem.*, 1932, **13**, 241; *A.*, 1016.

[23] *Ges. Abhandl. Kennt. Kohle*, 1930, **9**, 27; *A.*, 360.

[24] *N.Z. J. Sci. Tech.*, 1931, **12**, 284; *A.*, 1931, 951, 1030.

A critical review of the published theories of coal formation is given by E. Berl, A. Schmidt, and H. Koch.[25]

Petroleum is regarded by A. F. von Stahl[26] as related to the occurrence of hydrogen sulphide springs, which are attributed to the decomposition of proteins. K. Kobayashi[27] assigns the origin of Japanese petroleum to the distillation of buried fish remains by volcanic action under the sea, followed by absorption in acid clays. Chemical aspects of petroleum formation have been discussed by S. C. Lind.[28]

Contributions to the description of coal have been made by H. Briggs,[29] who finds a graphical relation between the oxygen and carbon contents of fusain, etc. Resin in coals is described by K. A. Jurasky[30] and H. Steinbrecher;[31] E. Hoffmann and H. Kirchberg[32] give a detailed account of resin inclusions in a Ruhr coal. Brown coals containing fibrous lignite, residues of the bark of conifers, are described by W. Gothan and Benade.[33] Contrary to views expressed by E. Berl and others (above), G. Stadnikow[34] describes a Siberian coal seam, free from metamorphism, in which the upper layers are typical brown coals, the lower being bituminous, suggesting the transformation of brown coal into bituminous.

Meteorites.

Small pieces of siliceous glass known as tektites have been found in Indo-China, Malay, North Borneo, and the Philippines; the composition is remarkably uniform, with about SiO_2, 70; Al_2O_3, 12; FeO, 5% etc., and they are believed by A. Lacroix[35] to be of meteoric origin. A. R. Alderman[36] has described meteor craters from Henbury, Australia; glassy fused rock was found, with large numbers of iron fragments. Among meteorites recently described may be mentioned an iron meteorite from Mexico,[38] containing over 16% of nickel, an amount also found in the Hoba (Grootfontein) meteorite,[39] which is the largest known. Other irons are described by H. H. Nininger,[40] L. L. Fermor,[41] C. Palache and F. H. Gonyer,[42] D. R. Grantham and F. Oates.[43]

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[25] *Angew. Chem.*, 1932, **45**, 517; *A.*, 1016.

[26] *Petroleum*, 1931, **8**, 145; *A.*, 1931, 460.

[27] *J. Soc. Chem. Ind. Japan*, 1931, **34**, 102.

[28] *Science*, 1931, **73**, 19; *A.*, 1931, 332.

[29] *Proc. Roy. Soc. Edin.*, 1932, **52**, 195; *A.*, 716.

[30] *Brennstoff-Chem.*, 1931, **12**, 161; *A.*, 1931, 818.

[31] *Ibid.*, 1931, **12**, 163; *A.*, 1931, 818.

[32] *Ibid.*, 1930, **11**, 389.

[33] *Braunkohle*, 1930, **29**, 274; *A.*, 1931, 60.

[34] *Brennstoff-Chem.*, 1932, **13**, 101; *A.*, 597.

[35] *Compt. rend.*, 1930, **191**, 893; 1931, **192**, 265, 1685; *A.*, 1931, 1146; 1932, 1028.

[36] *Min. Mag.*, 1932, **23**, 19.

[38] *Amer. J. Sci.*, 1931, [v], **22**, 360.

A. R. Crook and O. C. Farrington [44] describe a meteorite with high (Fe,Mg)O. A pallasite from Central Australia [45] contains fragmental olivine; E. S. Simpson and D. G. Murray [46] describe a siderolite containing large crystals of dark olivine and greyish-white enstatite. A fragment from S. E. Arabia described by W. Campbell Smith [47] has the same minerals in chondrules with some glass and felspar; in a special method of analysis by M. H. Hey the metals are separated by heating the powder in a current of dried chlorine.

A. F. HALLIMOND.

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[39] L. J. Spencer, *Min. Mag.*, 1932, **23**, 1; *A.*, 359; also S. G. Gordon, *Proc. Acad. Nat. Sci. Philadelphia*, 1931, **83**, 251.

[40] *Amer. J. Sci.*, 1931, [v], **22**, 69; *Amer. Min.*, 1932, **17**, 221, 396; *A.*, 1230.

[41] *Rec. Geol. Survey India*, 1931, **65**, 161; *A.*, 1931, 1265.

[42] *Amer. Min.*, 1932, **17**, 357.

[43] *Min. Mag.*, 1931, **22**, 487; *A.*, 1931, 1028.

[44] *Trans. Ill. Acad. Sci.*, 1930, **22**, 442; *A.*, 1931, 1389.

[45] L. J. Spencer, *Min. Mag.*, 1932, **23**, 38; *A.*, 359.

[46] *Ibid.*, p. 33; *A.*, 359.

[47] *Ibid.*, p. 43; *A.*, 359.

SUB-ATOMIC PHENOMENA AND RADIOACTIVITY.

The important work of the two years (1931—32) under review has again for the most part been physical in nature; it has been an eventful time for nuclear physics. A new, possibly ultimate, particle, the neutron, has been discovered, and it has already proved to be a useful weapon in investigations on nuclear structure; it has been eagerly seized on by theorists interested in the structure of the atom. It has been found that protons when generated with sufficiently high velocities may bring about nuclear disintegration by bombardment similar to that effected by the α-particle. The neutron may also act as a projectile in a similar way. Many new isotopes of non-radioactive elements have been found, and their masses determined with a greater exactness than heretofore. In this work the magnetic-spectrograph and the ordinary spectroscope are assisting the mass-spectrograph more and more as instruments of investigation; the most remarkable isotope found during the period, that of hydrogen with a mass of 2, falls to the credit of band-spectrum analysis. This combination of methods appears to be so promising as probably to render superfluous in the near future the older chemical methods of determining atomic weights. There has been a considerable advance in knowledge of the origin of the γ-ray, especially in its relation to the rare, high-velocity, α-particle; also of the properties of the penetrating radiation, although its exact nature and origin still elude investigators. On the chemical side, the simplicity that ascribed all α-particle radioactivity to atoms of high atomic number has been surprisingly disturbed in two ways. Element 87, apparently without detectable radioactivity, has been detected both by *X*-ray analysis and by the magnetic-spectrograph, while samarium of atomic number 62 has been found to be radioactive, expelling α-particles.

Radioactivity of Samarium.

G. von Hevesy and M. Pahl [1] have made preliminary observations on the radioactivity of the rare-earth element samarium (at. wt. 150·4). This is of the α-particle type; consequently, samarium is the first element outside the range of heavy elements thallium–uranium to show this type of activity. A layer of samarium oxide has an activity of about one-third of that of a thick layer of potassium chloride of equal surface. The radiation is reduced to half-value by aluminium of thickness 1·3 μ. Preparations from different sources showed the same specific activity. Chemical purification indicated that the activity is not due to known radioactive elements; it is suggested, however, that it may be due to the very rare element 61, to which it is chemically very similar.

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[1] *Nature*, 1932, **130**, 846.

Discovery of Element 87.

Despite the extreme unlikelihood[2] of the existence of elements 85 and 87 in nature, on account of the known instability of the neighbouring elements 88, 86, and 84, two pieces of evidence have been put forward to support the existence of the missing member of the alkali metals. J. Papish and E. Wainer[3] worked up 10 kg. of samarskite rich in uranium, containing rubidium and cæsium, so as to concentrate the last. The X-ray lines $M\alpha_1$, $L\alpha_1$, $L\alpha_2$, $L\beta_2$, and $L\eta$, calculated from Moseley's diagram for element 87, were found in the concentrate on excitation in a Siegbahn apparatus of high dispersion; the $L\beta_2$ line, for example, calculated to be 0·8524, was found as 0·853 Å. The element is regarded as non-radioactive or very feebly radioactive; radioactivity, however, has yet to be studied in detail. L. L. Barnes and R. C. Gibson[4] have found independent evidence of the new element by examining with a Dempster magnetic-spectrograph alkali sulphates known from X-ray examination to contain traces of element 87. A mass of 220 ± 1 was the only one which could not be assigned to known elements. Now it is known on general grounds that the isotopes of element 87 would be 221 and 223 or 221 and 219, an element of odd atomic number having a maximum of two isotopes each of odd atomic mass. The mass found is therefore confirmatory of the existence of the new element, which can thus be provisionally assigned masses of 219 and 221 or, if simple, a mass of 219 or of 221. F. Allison, (Miss) E. R. Bishop, A. L. Sommer, and J. H. Christensen[5] have described experiments with a magneto-optical method, depending on the time-lag differences of the Faraday effect behind the magnetic field, on solutions of minerals. In solutions of pollucite and lepidolite, minima were observed attributed to element 87. Six minima are considered to indicate the probable existence of element 85 also. They have sufficient confidence in their observations to give names to these two elements, but this is not yet shared by other workers. Preparations found to contain comparatively large amounts of element 87 by the magneto-optical methods were found not to contain it by *X*-ray examination.[3] Further, when the method has been applied in a region where the results are well attested, as for example to the complexity of copper [6] or tantalum,[5, 7, 19] the results are at variance with those obtained by the mass-spectrograph. It is extremely unlikely also that an element of odd atomic number, like number 85, has more than two isotopes.

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[2] *Ann. Reports*, 1928, **25**, 317.

[3] *J. Amer. Chem. Soc.*, 1931, **53**, 3818; *A.*, 1931, 1348.

[4] *Physical Rev.*, 1932, [ii], **40**, 318.

[5] *J. Amer. Chem. Soc.*, 1932, **54**, 613; *A.*, 317; F. Allison and E. J. Murphy, *Physical Rev.*, 1930, [ii], **36**, 1097. See *ibid.*, **35**, 285; *A.*, 1931, 1391; *J. Amer. Chem. Soc.*, 1932, **54**, 405, 616; *A.*, 353, 355.

Isotopes and Mass-Spectra.

During the period knowledge of the isotopic composition of twenty-one elements has been extended. The results are summarised in Tables I and II. In the latter, mean atomic weights

TABLE I.

Element.	Atomic number.	Minimum number of isotopes.	Masses (nearest integer) of isotopes in order of abundance.
Hydrogen	1	2	1, 2
Beryllium	4	2	9, 8
Neon	10	4	20, 22, 21, 23
Scandium	21	1	45
Rubidium	37	2	85, 87
Strontium	38	3	88, 86, 87
Niobium	41	1	93
Ruthenium	44	(6)	102, 101, 100, 99, (98), 96
Cæsium	55	1	133
Barium	56	4	138, 137, 136, 135
Tantalum	73	1	181
Rhenium	75	2	187, 185
Osmium	76	6	192, 190, 189, 188, 186, 187
Mercury	80	9	202, 200, 199, 201, 198, 204, 196, 197, 203
Thallium	81	2	205, 203
Lead	82	8	208, 206, 207, 204, 209, 210, 203, 205,
Uranium	92	1	238

TABLE II.

Element.	Atomic number.	Packing fraction.	Calculated atomic weight (O = 16).	Internationa atomic weight.[7a]
Lithium	3	—	6·928 ± 0·008	6·94
Boron	5	—	10·794 ± 0·001	10·82
Scandium	21	− 7	44·96 ± 0·05	45·10
Zinc	30	− 9·9	65·38 ± 0·02	65·38
Niobium	41	*ca.* − 8	92·90 ± 0·05	93·3
Ruthenium	44	*ca.* − 6	101·1	101·7
Tin	50	− 7·3	118·72 ± 0·03	118·70
Cæsium	55	− 5 ± 2·0	132·92 ± 0·02	132·81
Tantalum	73	*ca.* − 4	180·89 ± 0·07	181·4
Rhenium	75	—	186·22 ± 0·07	186·31
Osmium	76	− 1 ± 2·0	190·31 ± 0·06	190·8
Thallium	81	1·8 ± 2	204·41 ± 0·03	204·39

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[6] (Miss) E. R. Bishop, *Physical Rev.*, 1932, **40**, 16; *A.*, 554.

[7] *J. Amer. Chem. Soc.*, 1931, **53**, 1627.

[7a] *J.*, 1933, 115.

of twelve elements, calculated from knowledge of the number of isotopes, their relative abundance, and their packing fractions, are compared with the International values ($O = 16$).

The new isotope of hydrogen was found by H. M. Urey, F. G. Brickwedde, and G. M. Murphy.[8] If isotopes H^2 and H^3 exist, it is expected thermodynamically that they should be concentrated when hydrogen is evaporated near the triple point. In specimens so concentrated, faint Balmer-spectrum lines were found at the calculated positions for H^2 as broad doublets after an exposure 400 times the normal one. No trace of H^3 was found. The abundance of H^2 to H^1 in ordinary hydrogen was estimated as 1 : 4000. W. Bleakney[9] found this ratio in ordinary electrolytic hydrogen as 1 : 30,000 ± 20%. H. Kallmann and W. Lasarev[10] found the abundance of ions of mass 3 to those of mass 2 at low pressures by a spectrographic method as 1 : 4000. Working with enriched hydrogen, K. T. Bainbridge[11] determined the mass of the new isotope as 2·01351 ± 0·00018 ($O^{16} = 16$) by comparing the positions of $H_2^1H^{2+}$ and He^+ on a microphotometer record; he deduced the binding energy of H^2 according as it is imagined as built up of two protons and one electron or one proton and one neutron. N. S. Grace[12] deduced theoretically the mass as 2·0113 ± 0·0012. E. W. Washburn and H. C. Urey[13] found that H^2 was easily concentrated by the fractional electrolysis of water; the residual water of cells which have operated for a few years contained a marked increase in abundance of H^2 relative to H^1. In the infra-red absorption spectrum of hydrogen chloride, band lines corresponding with H^2Cl^{35} and H^2Cl^{37} have been found by J. D. Hardy, E. F. Barker, and D. M. Dennison[14]; the abundances of H^2Cl in ordinary and in enriched hydrogen chloride were found to be 1 : 35,000 and 1 : 3500 respectively and the mass of H^2 was deduced as 2·01367 ± 0·0001 in satisfactory agreement with other provisional values. The ease with which H^2 can be concentrated in ordinary hydrogen marks it off sharply from all other isotopic mixtures; the result is to be expected in view of the relatively enormous difference between the two isotopic masses. That H^2 could exist at all would have been regarded as most extraordinary had not the neutron[15] almost simultaneously been found.

Although H^3, He^3, and He^5 have been sought and not found,[9] there is some evidence for Be^8. W. W. Watson and A. E. Parker [16] found weak satellites in the band spectrum of beryllium hydride which they ascribe to Be^8; the relative intensities of the hydrides of Be^8 and Be^9 were estimated as 1 : 2000. A fourth isotope of neon, Ne^{23}, is claimed by G. Hertz.[17] He succeeded in raising the ratio of Ne^{20} to Ne^{22}, normally 10 : 1, to 100 : 1 and in lowering it to 10 : 8, by a diffusion process. In a mixture of the latter ratio Ne^{23} in addition to Ne^{21} was indicated by mass-spectrographic but not by optical methods. This result, if corroborated, would be a remarkable one. Isobares of odd atomic weight are rare and the mass 23, common to neon and sodium, would have the added distinction of being the lightest isobare known. The remainder of the results of Table I are due to F. W. Aston, obtained often by ingenious and unexpected means in the face of great experimental difficulties. (Thus, rhenium heptoxide failed to give mass lines either as vapour or as solid. When gold chloride was excited in the tube containing rhenium oxide on the walls, rhenium lines were obtained in great intensity in absence of gold lines. Again, the intensity of oxygen lines was greatly enhanced by exciting them in a mixture containing helium.) Scandium,[18] niobium,[19] cæsium,[20] tantalum,[19] and uranium [21] have been found to be simple. The controversy [22] about the true atomic weight of cæsium seems now to be decided against the chemical methods. K. T. Bainbridge,[23] using Dempster's method of analysis, has shown that the abundance of a second isotope must be less than 0·3% of that of Cs^{133}; F. W. Aston,[20] by producing anode rays of cæsium and gas rays of xenon in the same tube, compared their masses to 1 part in 10^7 parts and proved conclusively that the packing fraction of cæsium has a normal value; his result is given in Table II. A similar dispute about tellurium is not yet settled. F. W. Aston's [24] value, 128·04, may be too high. O. Hönigschmid's [25] new determination by analysis of $TeBr_4$, 127·587 ± 0·019, is in agreement with the International value. There is a possibility that minor and light isotopes of tellurium [26] may bring down the higher value. The results on scandium, niobium, and tantalum suggest (Table II) that the chemical atomic weights are in each case a little too high. The simplicity of uranium is provisional; no second isotope of abundance greater than 2% of U^{238} could be detected. Rubidium [18] has been found to have its expected composition; a third isotope has been found for strontium [18] and a fourth for barium.[18] Ruthenium [27] and osmium [27] were each found to have six isotopes; the abundance of Ru^{98} is not yet decided. Rhenium [28] and thallium [18, 21] both have their heavier isotope in greater abundance, thus differing from all other complex elements of odd atomic number greater than 7. Two minor isotopes have been found for mercury [29] and four for lead.[30] Hg^{196} is certain, Hg^{203} probable; the former's abundance is approximately 0·01%, the latter's 0·006%. Of the four new lead isotopes, Pb^{203} and Pb^{205} are not certain; Pb^{207} and Pb^{210} are related in abundance to Pb^{208} as 19 : 1 : 250 according to F. W. Aston,[30] or as 8 : 1 : 200 according to K. Murakawa.[31] Pb^{204} has been found also by H. Schüler and E. G. Jones [32] in the hyperfine spectrum of ordinary lead. If Pb^{203} and Zr^{96} be confirmed, the mass 203 will share with mass 96 the rare property of belonging to three elements: Hg^{203}, Tl^{203}, Pb^{203} and Zr^{96}, Mo^{96}, Ru^{96}, respectively.

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[8] *Physical Rev.*, 1932, [ii], **40**, 1; *A.*, 554. [9] *Ibid.*, **41**, 32; *A.*, 894.

[10] *Naturwiss.*, 1932, **20**, 206, 472; *A.*, 442, 790.

[11] *Physical Rev.*, 1932, [ii], **42**, 1; *A.*, 1185.

[12] *J. Amer. Chem. Soc.*, 1932, **54**, 2562; *A.*, 790.

[13] *Proc. Nat. Acad. Sci.*, 1932, **18**, 496; *A.*, 894.

[14] *Physical Rev.*, 1932, [ii], **42**, 279.

[15] J. Chadwick, *Nature*, 1932, **129**, 312; *A.*, 443.

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[16] *Physical Rev.*, 1931, [ii], **37**, 167; *A.*, 1931, 403.
[17] *Naturwiss.*, 1932, **20**, 493; *A.*, 790.
[18] *Proc. Roy. Soc.*, 1932, [*A*], **134**, 571; *A.*, 210.
[19] *Nature*, 1932, **130**, 130; *A.*, 895.
[20] *Ibid.*, 1931, **127**, 813; *A.*, 1931, 783.
[21] *Ibid.*, **128**, 725; *A.*, 1931, 1349.
[22] *Ann. Reports*, 1928, **25**, 305.
[23] *Physical Rev.*, 1930, [ii], **36**, 1668; *A.*, 1932, 5.
[24] *Ann. Reports*, 1926, **23**, 280; see *A.*, 1925, ii, 618.
[25] *Naturwiss.*, 1932, **20**, 659; *A.*, 980.
[26] K. T. Bainbridge, *Physical Rev.*, 1932, [ii], **39**, 1021.

In Table II all the results except that for boron have been obtained by F. W. Aston. There has been difference of opinion on the abundance ratio $Li^7 : Li^6$. From band-spectrum work W. R. van Wijk and A. J. van Kœveringe [33] find the value 7·2. On the mass-spectrograph F. W. Aston [34] found 10·2 ± 0·5, which is close to 14·9, obtained by M. Morand [35] with a heated anode, and to 10·5, obtained by H. Schüler [36] from hyperfine structure of the spectrum of Li^+. It is likely that the variation in intensities of spectral lines due to Li^6 and Li^7 respectively, with the conditions under which they are excited, as found by G. Nakamura and T. Schidei,[37] is partly the cause of the above differences. This does not occur with positive rays.[38] The atomic weight of lithium calculated from F. W. Aston's results is given in the table. The corresponding value for boron is calculated from A. Elliott's[39] abundance ratio $B^{11} : B^{10}$, 3·63 ± 0·02, for Chilean boron.

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[27] *Nature*, 1931, **127**, 233; *A.*, 1931, 280. [28] *Ibid.*, p. 591; *A.*, 1931, 666.

[29] *Ibid.*, 1932, **130**, 847. [30] *Ibid.*, **129**, 649; *A.*, 554.

[31] *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1932, **18**, 245; *A.*, 892.

[32] *Nature*, 1932, **129**, 833; *A.*, 670.

[33] *Proc. Roy. Soc.*, 1931, [*A*], **132**, 98; *A.*, 1931, 992; *Naturwiss.*, 1931, **17**, 894; *A.*, 1931, 1348.

[34] *Nature*, 1931, **128**, 149; *A.*, 1931, 994.

[35] Thesis, Paris, 1927; *Compt. rend.*, 1926, **182**, 460; *A.*, 1926, 331.

[36] *Naturwiss.*, 1931, **19**, 772; *A.*, 1931, 207.

[37] *Japanese J. Physics*, 1931, **7**, 33; *A.*, 667; *Nature*, 1931, **128**, 759; *A.*, 1931, 1348.

[38] K. T. Bainbridge, *J. Franklin Inst.*, 1931, **212**, 317; *A.*, 1931, 1207.

Despite S. Meyer's[40] advocacy of the value $O^{16} = 16·0000$ as the best standard for chemical atomic weights, the International Union for Chemistry,[41] guided largely by F. W. Aston,[42, 44] has wisely decided not to depart from the conventional and practical standard, $O = 16$, at present in existence, for it is very probable that the abundances of O^{16}, O^{17}, and O^{18} in nature is so invariable that the mean atomic mass of the oxygen atom is as precise a constant as that of O^{16}. For purposes of atomic and nuclear structure, radioactivity, mass-spectrography, etc., where a precision of 1 in 10^5 is desirable and is expected to be attained, the neutral atom $O^{16} = 16·0000$ has been chosen from its competitors as standard by the International Radium-Standards Committee.[43] The ratio of a mass on this physical standard $O^{16} = 16$ to that on the other—the Naudé correction—has been hitherto taken as 1·000125.[47] New determinations of this constant have been made by R. Mecke and W. H. J. Childs[45] and by F. W. Aston.[46] The former find the relative abundances $O^{16} : O^{17} : O^{18}$ as (630 ± 20) : 0·2 : 1, the latter as 536 : 0·25 : 1. These values raise S. M. Naudé's correction to approximately 1·0002, an alteration which can, of course, have a trifling effect only on the values of atomic weights calculated from mass-spectrograph data, such as are given in Table II. The relative abundance $N^{15} : N^{14}$, given earlier as 1 : 700, has been determined as 1 : 346 by G. M. Murphy and H. C. Urey.[48]

The Neutron.

The existence of a neutron, possibly an ultimate particle, of mass approximately 1 and charge zero, was mooted by J. Chadwick[15] as the simplest interpretation of a series of observations initiated by W. Bothe and H. Becker,[49] which were continued and followed up by (Mme.) I. Curie[50] and F. Joliot,[51] by H. C. Webster,[52] and finally by himself. Beryllium under bombardment by α-particles did not emit protons as did boron or nitrogen, but gave out a weak radiation more penetrating than any γ-radiation known. This when examined by ionisation methods caused material containing combined hydrogen to emit swift protons. The explanation suggested for this striking occurrence was that the protons had gained their energy by a radiation recoil in a process similar to the Compton effect with electrons; the quantum energy of the radiation was accordingly deduced. J. Chadwick [15, 53] found that swift recoil atoms were liberated when the radiation traversed not only hydrogen-containing material but also helium, lithium, carbon, air, and argon. His results showed that, if energy and momentum were conserved in these encounters, the quantum hypothesis of the radiation emitted would not hold; the existence of the neutron was the simplest explanation of the facts. A neutron in motion would be expected to produce little if any ionisation in passing through matter and to indicate its presence by the recoil of an atomic nucleus with which it collided. Such recoil nuclei would be expected to be easily detected in an ionisation chamber or in a Wilson expansion chamber. The velocity of recoil of a given atom would be expected to fall off when the radiation was passed through increasing thicknesses of an absorbing material such as lead. (This would not be expected if the radiation were a γ-radiation.) These expectations have been verified by J. Chadwick. The velocity of the neutron when it is liberated is estimated as one-tenth of that of light. Its mass is found as probably between 1·005 and 1·008, suggesting that the neutron may be a small dipole made up of proton and electron or even a proton embedded in an electron. Neutrons are found to be emitted by boron as well as from beryllium. The processes imagined are $Be^9 + He^4 \longrightarrow C^{12} + n^1$, $B^{11} + He^4 \longrightarrow N^{14} + n^1$, n^1 denoting the neutron and the other symbols the nuclei of the elements named. (It is from the second expression that J. Chadwick, taking cognizance of energies and masses, deduced the neutron's mass.) It is probable that other processes occur simultaneously, *e.g.*, $Be^9 + He^4 \longrightarrow C^{13} + \gamma$-radiation and $B^{10} + He^4 \longrightarrow N^{14} + \gamma$-radiation. N. Feather made an important advance in the work on neutrons by showing that they also could effect artificial disintegration. He obtained disintegration tracks in an expansion chamber resulting from collisions of neutrons with nitrogen [54] and with oxygen [55] which could be interpreted as $n^1 + N^{14} \longrightarrow He^4 + B^{11}$, the reverse of J. Chadwick's result, and as $n^1 + O^{16} \longrightarrow C^{13} + He^4$. There

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[39] *Nature*, 1930, **126**, 845; *A.*, 1931, 15; *Z. Physik*, 1931, **67**, 75; *A.*, 1931, 279.

[40] *Physikal. Z.*, 1932, **33**, 301; *A.*, 442.

[41] *Ber.*, 1932, **65**, [*A*], 33; *A.*, 554.

[42] *Nature*, 1931, **128**, 731.

[43] *Phil. Mag.*, 1931, **12**, 609; *A.*, 1931, 1108.

[44] *Ann. Reports*, 1930, **27**, 310.

[45] *Z. Physik*, 1931, **68**, 362; *A.*, 1931, 543.

[46] *Nature*, 1932, **130**, 21; *A.*, 894.

[47] *Ann. Reports*, 1930, **27**, 306.

[48] *Physical Rev.*, 1932, [ii], **41**, 141; *A.*, 980.

[49] *Z. Physik*, 1930, **66**, 289; *A.*, 1931, 142.

[50] *Compt. rend.*, 1931, **193**, 1412; *A.*, 210.

[51] *Ibid.*, p. 1415; *A.*, 210; *ibid.*, 1932, **194**, 273; *A.*, 210.

[52] *Proc. Roy. Soc.*, 1932, [*A*], **136**, 428; *A.*, 671.

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[53] *Proc. Roy. Soc.*, 1932 [*A*], **136**, 692; *A.*, 790.

[54] *Ibid.*, p. 709; *A.*, 790. [55] *Nature*, 1932, **130**, 237; *A.*, 981.

are with nitrogen other possibilities than the ejection of an α-particle: certainly the liberation of a proton, possibly the liberation of H^2. (Mme.) I. Curie and F. Joliot[56] find that neutrons may be emitted by lithium, that those emitted by beryllium form two groups, and that photons may be emitted simultaneously with neutrons; their results confirm the neutron hypothesis from a different angle. Further confirmation comes from the work of F. Rasetti[57] and of J. L. Destouches.[60] The excitation of neutrons by radon and their transmission through matter has been studied by M. de Broglie and L. Leprince-Ringuet,[58] and their penetrating power by J. Thibaud and F. D. La Tour.[59] The existence of neutrons and of H^2 has encouraged theorists to attempt to accommodate them in the nuclei of light atoms. H. C. Urey's scheme[61] preceded his experimental work.[8] Provisional schemes, independent but in some respects similar, have also been put forward by H. L. Johnston,[62] F. Perrin,[63] J. H. Bartlett,[64] E. G. Jones,[65] W. D. Harkins,[66] and others. In one of F. Perrin's schemes, the "demi-helion" is envisaged. This is a particle of mass 2 and charge 1, the union of proton and neutron, and known in the free state as the heavier isotope of hydrogen. The oldest scheme is due to W. D. Harkins.

Artificial Disintegration by Swift Protons.

J. D. Cockcroft and E. T. S. Walton[67] developed the technique of producing and using steady high potentials up to 600,000 volts. When lithium oxide was bombarded with a stream of protons, α-particles in pairs were found to be produced. The effect became appreciable when the protons had been accelerated beyond 120,000 volts; at 250,000 volts a disintegration particle was got for about every 10^9 protons striking the lithium. The process imagined is $Li^7 + H^1 \longrightarrow He^4 + He^4$, the symbols representing the nuclei of the elements named. A similar disintegration was found to occur less readily with boron and fluorine, appreciably less with uranium, aluminium, and carbon, and to a very slight extent with a few other elements. The processes here provisionally imagined are $B^{11} + H^1 \longrightarrow He^4 + Be^8$ or $3He^4$, $F^{19} + H^1 \longrightarrow He^4 + O^{16}$, $Al^{27} + H^1 \longrightarrow He^4 + Mg^{24}$, etc., the nature and mass of the residual atom being such that atomic mass and atomic number are conserved in the process. It may be significant that the elements which suffer the emission of the α-particle most easily have masses of form $4a+3$, a being an integer, *i.e.*, have nuclei presumably made up of 3 protons and 2 electrons in addition to more stable units. It is reasonable to suppose that the capture of a proton in such nuclei might result in the formation and expulsion of an α-particle from it. To sum up : Originally, artificial disintegration of light atoms consisted only in the production of protons by swift α-particles. Now α-particles have been shown to produce neutrons. Each of these processes can also occur in reverse; protons can produce α-particles, neutrons can produce α-particles. Neutrons can, in addition, produce protons, but the inverse process has not yet been demonstrated. Not less in importance is the nature of the resultant residual atom. When the α-particle is the projectile, the resultant atom is of higher atomic number than that bombarded; when neutrons or protons bombard, it is of lower atomic number.

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[56] *Nature*, 1932, **130**, 57; *A.*, 895.

[57] *Naturwiss.*, 1932, **20**, 252; *A.*, 556.

[58] *Compt. rend.*, 1932, **194**, 1616; *A.*, 672; *Nature*, 1932, **130**, 315; *A.*, 1073.

[59] *Compt. rend.*, 1932, **194**, 1647; *A.*, 672.

[60] *Ibid.*, p. 1909; *A.*, 672.

[61] *J. Amer. Chem. Soc.*, 1931, **53**, 2872; *A.*, 1931, 1108; *Nature*, 1932, **130**, 403; *A.*, 1074.

[62] *J. Amer. Chem. Soc.*, 1931, **53**, 2866; *A.*, 1931, 1108.

[63] *Compt. rend.*, 1932, **194**, 1343, 2211; *A.*, 556, 790.

[64] *Nature*, 1932, **130**, 165; *A.*, 894.

[65] *Ibid.*, p. 580; *A.*, 1187.

[66] *J. Amer. Chem. Soc.*, 1932, **54**, 1254; *A.*, 556; *Nature*, 1933, **131**, 23.

[67] *Nature*, 1932, **129**, 649; *A.*, 556; *Proc. Roy. Soc.*, 1932, [*A*], **137**, 229 *A.*, 893; *Nature*, 1933, **131**, 23.

Radioactive Constants, Fundamental Constants, and Other Data.

A complete survey of radioactive and other atomic constants has been made by the International Radium-Standards Committee.[43] They give as masses H = 1·0078, proton = 1·0072, He = 4·00216, α-particle = 4·00106, and the electron = 0·000548 (O^{16} = 16·0000); (on this scale, unity weighs $1{\cdot}649 \times 10^{-24}$ g.); Avogadro's constant is given as $6{\cdot}0644 \times 10^{23}$ or $6{\cdot}0265 \times 10^{23}$ according as $e = 4{\cdot}770 \times 10^{-10}$ or $4{\cdot}80 \times 10^{-10}$, the former being preferred. The number of α-particles expelled per second by 1 g. of radium (free from products) is taken as $3{\cdot}70 \times 10^{10}$, and the ratio of radium to uranium in minerals as $3{\cdot}4 \times 10^{-7}$. In a few cases alternative values are given for the half-periods of radioactive products; *e.g.*, 5·0 and 4·9 days for radium-*E* and 24·5 and 23·8 days for uranium-X_2. $3{\cdot}0 \times 10^5$ Years is recommended for uranium-II, the direct measurement agreeing with the value deduced from Geiger and Nuttall's relation. C. H. Collie [68] has, however, since shown, as the result of three concordant experiments, that the half-period of this product must be at least a million years. He separated electrolytically the uranium-II arising from the decay of a known quantity of uranium-X and counted the α-particles from the source electrically. O. Gratias and C. H. Collie[69] found the half-period of uranium-Y to be 24·0 ± 0·58 hours, the accepted value, 24·6, being ascribed to lack of saturation in the electroscopes used in decay measurements. New determinations of the half-period of uranium-X_1 and of the actinium–radium branching ratio from uranium by E. Walling[70] confirm the International values, the higher alternative in the first case. A. F. Kovarik and N. I. Adams[71] confirm the International values for the radium–uranium ratio in minerals and the actinium–radium ratio; they obtain directly the half-period of uranium-I as $4{\cdot}52 \times 10^9$ years, 3% higher than the International value. F. Soddy,[72] from the growth of radium in uranium purified 25 years ago, finds the half-period of ionium as $7{\cdot}41 \times 10^4$ years, 12% less than the International value.

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[68] *Proc. Roy. Soc.*, 1931, [*A*], **131**, 541; *A.*, 1931, 891.

Great progress has been made in the analysis of groups of α-particles both by the electrical counting methods employed at Cambridge[73] and by the magnetic deviation method used in Paris.[73] (Lord) Rutherford, F. A. B. Ward, and W. B. Lewis[74] have found that the long-range α-particles from radium-C' may be analysed into nine homogeneous groups of ranges 7—12 cm. The most abundant of these groups has 16·7 particles per million of the ordinary group of range 6·96 cm., the remainder have abundances varying from 0·2 to 1·27 per million. (Lord) Rutherford, C. E. Wynn-Williams, and W. B. Lewis[75] find two groups of long-range particles from thorium-C', of ranges 9·78 and 11·66 cm., in a ratio 1 : 5·6, the long-range particles having an abundance relative to the ordinary group of range 8·62 cm., of 1·9 per million. (S. Rosenblum[73] had found them even more complex and since then has extended[76] his result.) The earlier work[73] on the complexity of the particles from actinium-C was confirmed; actinium-C has two groups in relative abundance 0·19 and 1, and relative velocity 0·9737 and 1. The values for the homogeneous group from actinium-C' are on this scale 0·0032 and 1·062 respectively. The relative velocities have been confirmed by (Mme.) P. Curie and S. Rosenblum,[77] who find 0·973 : 1 : 1·062. W. B. Lewis and C. E. Wynn-Williams[78] have analysed the particles from actinon into two groups, the complexity with this product being similar to that with actinium-*C*, with regard to both relative numbers and relative velocities. As (Mme.) I. Curie [79] had found that the α-particles from radioactinium consist of two groups in about equal numbers, it would appear that there is some recurring characteristic of the nucleus underlying this phenomenon. (Mme. P. Curie and S. Rosenblum,[80] however, have found that radioactinium is more complex than has been supposed. Its particles have six or seven groups, two of which are very strong, two strong, and the remainder weak. Actinium-*X*, however, was found to have two groups of particles.) S. Rosenblum and (Mlle.) C. Chamié [81] have found that radiothorium emits two and possibly three groups of particles, and S. Rosenblum [82] found two groups from radium itself. During these investigations, actinium-*A*, thoron, thorium-*A*, radon, and radium-*A* were found to give homogeneous particles; many determinations of ranges and energies of α-particles from every product except uranium, protoactinium, and thorium have been recorded there and elsewhere.[83] The accepted values of the ranges of uranium-I, thorium, and uranium-II have been confirmed by F. N. D. Kurie,[84] G. H. Henderson and J. L. Nickerson,[85] and S. Bateson [86] respectively.

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[69] *Proc. Roy. Soc.*, 1932, [*A*], **135**, 299; *A.*, 443.

[70] *Z. Physik*, 1932, **75**, 425, 432; *A.*, 555.

[71] *Physical Rev.*, 1932, [ii], **40**, 718; *A.*, 790.

[72] *Phil. Mag.*, 1931, **12**, 939; *A.*, 5.

[73] *Ann. Reports*, 1930, **27**, 313.

[74] *Proc. Roy. Soc.*, 1931, [*A*], **131**, 684; *A.*, 1931, 890.

[75] *Ibid.*, **133**, 351; *A.*, 1931, 1349.

[76] *Compt. rend.*, 1931, **193**, 848; *A.*, 5.

[77] *Ibid.*, p. 33; *A.*, 1931, 995.

[78] *Proc. Roy. Soc.*, 1932, [*A*], **136**, 349; *A.*, 671.

Evidence that the emission of γ-rays from radium-*C′* is intimately connected with the occurrence of its groups of long-range particles was given by (Lord) Rutherford, F. B. Ward, and W. B. Lewis; [74] it was concluded that the γ-rays arise from the transition of an α-particle in an excited nucleus between two levels of different energies. This question has been discussed in more detail by (Lord) Rutherford and C. D. Ellis,[87] C. D. Ellis,[88] and (Lord) Rutherford and B. V. Bowden.[89] For radium-*C′* it is supposed that in the preceding transformation the emission of an α-particle causes a violent disturbance in the resulting nucleus which causes some of the constituent α-particles to be raised to a much higher level than the normal. These, being unstable, are believed to fall back after a very short interval to normal level, emitting their surplus energy as γ-radiation of definite frequency. The ideas of wave mechanics, however, suggest that in this short interval there is a small chance that some of the α-particles in the higher states can escape from the nucleus. On this view the escaping α-particles are the long-range particles observed, and their energies give the values of the energy level in the nucleus which they occupied before escape. It was, in fact, found that the differences of energies between the various groups of α-particles were closely connected with the energies of the most prominent γ-rays in the spectrum, and, in general, strong evidence was found that γ-rays have their origin in the transitions of one or more α-particles in an excited nucleus. The energies set free in transitions are given approximately by the expression $E = pE_1 - qE_2$, where E_1 is a difference in energy of two states, E_2 a smaller difference of interaction, and p and q integers. Forty γ-rays from radium-C' and a smaller number from radium-B can be conveniently expressed by such an equation.

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[79] *Compt. rend.*, 1931, **192**, 1102; *A.*, 1931, 783.

[80] *Ibid.*, 1932, **194**, 1232; *A.*, 555.

[81] *Ibid.*, p. 1154; *A.*, 555.

[82] *Ibid.*, **195**, 317; *A.*, 895.

[83] S. Rosenblum and G. Dupouy, *Compt. rend.*, 1932, **194**, 1919; *A.*, 671: G. H. Briggs, *J. Sci. Inst.*, 1932, **9**, 5; *Nature*, 1932, **130**, 1000.

[84] *Physical Rev.*, 1932, [ii], **41**, 701; *A.*, 1186.

[85] *Ibid.*, 1930, [ii], **36**, 1344; *A.*, 1931, 16.

[86] *Canadian J. Res.*, 1931, **5**, 567; *A.*, 106.

[87] *Proc. Roy. Soc.*, 1931, [*A*], **132**, 667; *A.*, 1208.

[88] *Ibid.*, 1932, [*A*], **136**, 396; *A.*, 671.

[89] *Ibid.*, p. 407; *A.*, 671.

The connexion between α-particles and γ-rays in thorium-C is different. With radium-C' the most intense α-particle has the lowest energy and the long-range particles are rare occurrences; this is not so with thorium-C. G. Gamow has proposed that here the thorium-C nucleus is initially formed with all the α-particles in the ground state, not, as with radium-C', with some of the α-particles in higher levels of energy, and that disintegration can sometimes occur in such a way as to leave the *product nucleus* excited. C. D. Ellis [88] found that the γ-rays were emitted immediately after the disintegration of thorium-C, in agreement with G. Gamow's [90] theory. This provides further proof of the connexion of γ-rays with excited α-particle states in the nucleus. After the discovery that actinon emits two distinct groups of α-particles, it was found by (Lord) Rutherford and B. V. Bowden [89] that the transformation actinon ⟶ actinium-A was accompanied by weak β-rays and strong γ-rays. From the measurement of the penetrating power of the latter, it was concluded that the energy of the γ-rays is of the right order to be expected from the difference of energies of the α-particle groups; again, strong confirmatory evidence that γ-rays have their origin in transitions of α-particles in an excited nucleus.

The controversy as to the most probable values of the fundamental constants, e, h, and the reciprocal of the fine-structure constant, $2\pi e^2/hc$, continues. W. N. Bond [91] has developed a new way of reducing the experimental data used in connexion with the determinations of e and h which is based on the observation that each group of experiments connects h and e by an equation of the form $h = Ae^n$, where n is 1, 4/3, or 5/3 according to the experiments. He gives to e, h, and $hc/2\pi e^2$ respectively (significant figures only) the values 4·779, 6·558, and 137·02. From the same data, however, R. T. Birge[92] gets 4·769, 6·544, and 137·31. F. Kirchner [93] gets 4·798, 6·615, and 137·09 or 4·782, 6·577, and 137·25, depending upon which alternative data, derived from measurements of the short-wave limit of the X-ray spectrum, are taken. K. Shiba [94] has also critically reviewed the available data. He argues that the X-ray value of e gives consistent values of h by eight methods. His values are $e = 4{\cdot}803$, $h = 6{\cdot}624$, and $hc/2\pi e^2 = 137{\cdot}03$. There is still, therefore, at the present level of accuracy of measurement, a case for (Sir) A. S. Eddington's theory,[95] which requires for the reciprocal of the fine-structure constant the exact value 137. There appears to be little, however, for his other theory,[96] which requires for the ratio of the masses of proton and electron the value 1849·6.

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[90] *Nature*, 1930, **126**, 397; *A.*, 1339.

[91] *Proc. Physical Soc.*, 1932, **44**, 374; *A.*, 672; *Nature*, 1931, **127**, 557; *A.*, 1931, 667; *Phil. Mag.*, 1930, **10**, 994; *A.*, 1931, 143; *ibid.*, 1931, **12**, 632; *A.*, 1931, 1207; *Physical Rev.*, 1932, [ii], **41**, 368.

Chemistry of Protoactinium.

A. V. Grosse[97] has continued his work[98] on the chemistry of protoactinium, working with 10—50 mg. of pentoxide free from other metals. It has been generally assumed that the pentoxides of tantalum and protoactinium are chemically very similar, as are, for example, the corresponding compounds of barium and radium. They are, however, widely different. Protoactinium is definitely basic, as it should be from its position in the periodic classification, whereas tantalum is feebly acidic. They are similar in that both oxides dissolve in 40% hydrofluoric acid and are precipitated by ammonia from mineral acid solutions. Protoactinium oxide is insoluble in molten potassium carbonate (in which tantalum oxide is completely soluble), and almost entirely soluble in molten sodium bisulphate (in which tantalum is nearly insoluble). Protoactinium is precipitated from acid solutions by excess of phosphoric acid; there is no corresponding precipitation with tantalum. The separation is, in consequence, a simple matter. O. Gratias [99] has independently made similar observations with unweighably small quantities of protoactinium; he used an amplifier and an ionisation counter to detect the radioactive material's presence in the chemical operations. He showed that the product of decay of uranium-Y emitted α-particles, and had approximately the same half-period and the same chemical properties as protoactinium. He has thus established directly by experiment what hitherto has been merely assumed on general grounds, namely, that uranium-Y is the direct parent of protoactinium.

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[92] *Physical Rev.*, 1932, [ii], **40**, 228; *A.*, 672.

[93] *Ann. Physik*, 1932, [v], **13**, 59; *A.*, 556.

[94] *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1932, **19**, 97; *A.*, 1187.

[95] *Ann. Reports*, 1930, **27**, 323; *A.*, 1929, 231.

[96] *Proc. Camb. Phil. Soc.*, 1931, **27**, 15; *A.*, 1931, 279; *Ann. Reports*, 1930, **27**, 324.

[97] *J. Amer. Chem. Soc.*, 1930, **52**, 1742; *A.*, 1930, 883.

[98] *Ann. Reports*, 1928, **25**, 313.

[99] Thesis, Oxford, 1932; O. Gratias and C. H. Collie, *J.*, 1932, 987; *A.*, 443.

The Penetrating Radiation.

The problem [1] of the cosmic or penetrating radiation has definitely advanced towards solution during the period under review, although at first sight it would appear that opinion about it could hardly be more widely divided; its nature has been variously described as quantum, neutron, electron, and positively charged particle. There has been a gradual change, however, from the older quantum view of R. A. Millikan [2] to the view that the radiation is a very high-energy particle. The former view has been reconsidered by (Sir) J. H. Jeans,[3] who rejects the view that the radiation can be anything but γ-radiation on the grounds that a charged particle would be deflected in the laboratory by a magnetic field, which was apparently not the case,[4] and could not fall evenly on the earth, as it does,[5] owing to the influence of the earth's magnetic field. He has calculated the penetrating power of the radiation on the assumption of R. A. Millikan that part of it is generated by the formation of nuclei of iron from the necessary protons and electrons, and on his own assumption, by the annihilation of one proton or four protons by their respective electrons. In this calculation he has used the formula of O. Klein and Y. Nishina,[6] the scattering electrons being taken as *all* the electrons in the atom and not, as is generally done, the extra-nuclear electrons only. The two hardest constituents of penetrating radiation, as found by E. Regener,[7] have penetrating powers very close indeed to the calculated values on the assumption that four protons and one proton have been annihilated; the synthesis of iron gives much too soft a radiation in this calculation. (Sir) J. H. Jeans has pointed out that if the radiation had such an origin there is no need to assume, as R. A. Millikan has done, that the process is still occurring in the depths of space. It may be calculated that the hardest constituent of the radiation is so penetrating that it would not be reduced to $1/e$ of its initial intensity until after 5 × 10^{15} years, a period greater, so far as is known, than the age of the universe. The penetrating radiation of to-day may therefore be the result of the annihilation of matter (possibly near the surfaces of astronomical bodies, more probably in unattached atoms or molecules in free space) a remote period ago. A similar view has been tentatively advanced by E. Regener.[8]

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[1] *Ann. Reports*, 1930, **27**, 322. [2] *Ibid.*, 1928, **25**, 321.

[3] *Nature*, 1931, **128**, 104; **127**, 594; *A.*, 1931, 666.

[4] P. Epstein, *Proc. Nat. Acad. Sci.*, 1930, **16**, 658.

[5] K. Grant, *Nature*, 1931, **127**, 924. [6] *Ibid.*, 1928, **122**, 398.

[7] *Ibid.*, 1931, **127**, 233; *A.*, 1931, 408.

The replacement of the ionisation vessel by the Wilson cloud-chamber and the Geiger–Müller particle-counter has given results which have modified the above views. The newer workers regard the radiation as a particle. C. D. Anderson,[9] P. M. S. Blackett and G. Occhialini [10] and others [11] have devised apparatus so that the penetrating ray itself actuates the Wilson cloud-chamber, and a photograph of what is occurring may be taken at the time and not at random. In the device of P. M. S. Blackett and G. Occhialini the cloud-chamber is inserted between two Geiger–Müller counters in line. Passage of the penetrating radiation through both counters actuates the cloud-chamber within 0·01 sec., which is sufficient interval to enable the track to be photographed. They found that only about 10% of the tracks were markedly bent in a field of 2000 gauss, so that if the radiation was an electron its energy would be 10^6—10^7 volts. The remainder, unbent, corresponded with electrons of 6 × 10^8 volts or protons of 2 × 10^8 volts. C. D. Anderson found a much smaller proportion of unbent tracks; they were quite rare. He observed pairs of tracks frequently, one of which was always that of an electron. He ascribed these to the disruption of a single atomic nucleus by the penetrating radiation. Sudden bursts of ionisation, as though from a shower of ionising particles from a violently bursting nucleus, have been observed by E. G. Steinke,[12] H. Schindler,[13] A. H. Compton,[14] and others. These appear to be greater than those given by any α-particle and to be more frequent at high altitudes. The radiation also behaves peculiarly when it traverses successively thicknesses of two different metals; a peculiar secondary radiation is set up related to the primary as are δ-rays to α-particles. H. Geiger [15] interprets this puzzling occurrence by regarding the radiation as protons with very high energy. The older observation that the radiation comes equally from all parts of the sky has been confirmed.[16] While, however, V. F. Hess [17] has found that the sun does not contribute more than 0·5% of the total intensity at 2·5 km. above sea-level, A. H. Compton [18] found that the intensity at 3·9 km. was 1·5 ± 0·25% greater between 8 a.m. and 4 p.m. than between the corresponding night hours. The same observer,[19] in accord with J. Clay [20] but in discord with earlier observations,[5] found that the intensity of the radiation is in general higher the greater the angle of magnetic dip.

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[8] *Nature*, 1931, **127**, 859.

[9] *Physical Rev.*, 1932, [ii], **41**, 405.

[10] *Nature*, 1932, **130**, 363.

[11] L. M. Mott-Smith and G. L. Locher, *Physical Rev.*, 1931, [ii], **38**, 1399; 1932, **39**, 1883; *A.*, 5; T. J. Johnson, W. Fleisher, and J. C. Street, *ibid.*, 1932, **40**, 1048.

[12] *Physikal. Z.*, 1930, **31**, 1019; *Z. Physik*, 1932, **75**, 115; *A.*, 556.

[13] *Naturwiss.*, 1932, **20**, 491; *A.*, 791.

[14] *Physical Rev.*, 1932, [ii], **41**, 681.

[15] *Nature*, 1931, **127**, 785.

A. S. Russell.

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[16] E. Regener, *Nature*, 1932, **130**, 364; *Z. Physik*, 1932, **74**, 433; *A.*, 1072; A. Piccard, *Compt. rend.*, 1932, **195**, 71.

[17] *Nature*, 1931, **127**, 10; *A.*, 1931, 143.

[18] *Physical Rev.*, 1932, [ii], **41**, 111.

[19] *Ibid.*, p. 681.

[20] *Proc. K. Akad. Wetensch. Amsterdam*, 1930, **7**, 711.

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